A CORRELATION BETWEEN FRICTION REDUCTION AND MOLECULAR SIZE FOR THE FLOW OF DILUTE AQUEOUS POLYETHYLENE-OXIDE SOLUTIONS IN PIPES

by

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THESIS

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ABSTRACT

Pipe-friction factors for dilute aqueous polyethylene-oxide solutions in pipes of nominal diameters of ¼, 3/8, and 3/4 in. were measured over a two decade range of Reynolds numbers. In the transition region, the amount of drag reduction is dependent upon polymer concentration and wall shear stress as well as Reynolds number. For high Reynolds numbers, where the wall shear stress was high compared to the critical value, no diameter effect was noted. Intrinsic viscosity measurements, made on samples withdrawn from pipe flow, provided direct evidence that polymer degradation take place under flow conditions. Spectrographic measurements indicated that this degradation is mechanical (and not chemical). The relative volume of solution occupied by polymer molecules (represented by the volume of equivalent hydrodynamic spheres) is shown to be a dominant parameter governing the drag-reduction phenomenon for polyethylene-oxide solutions in pipe flow. It is further shown that the equivalent volume ratio may be used to normalize the pipe friction factors for various concentrations of different molecular-weight species of polyethylene-oxide.

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I. INTRODUCTION

Experimental observations that cannot readily be explained by existing and seemingly applicable models of nature present an exciting challenge to the scientist. When numerous potential applications are obvious, added incentive exists to search for a better understanding of the phenomenon. Such a set of circumstances apply to the phenomenon of "hydrodynamic drag reduction" induced by additives, where it has been observed that under certain circumstances the presence of small amounts of certain additives markedly alters the hydrodynamic flow characteristics--both in internal (e.g., pipes) and external (around bodies) flows.

The early reports of this phenomenon (Vanoni, [86], 1946; Toms, [83], 1948; Mysels, [53], 1949) were largely overlooked, and their ramifications unappreciated. The reports of Shaver and Merrill [73] and Dodge and Metzner [15] in 1959 reawakened interest in the problem. Then, in the early 1960's, the works of Pruitt and Crawford [59], Hoyt and Fabula [17,33] and Savins [65] greatly accelerated interest by making potential applications patently obvious.

There now exists in the literature a great number of papers concerning drag reduction. As a measure of the accelerated interest, the bibliography of Lumley's review article [40] in the December 1967 issue of "Applied Mechanics Reviews" contains 74 references -- all dated since 1965. A quick perusal of the bibliography shows that this interest traverses many disciplines.

While a much better understanding of the phenomenon now exists, the mechanism responsible for drag reduction is not yet understood -- if in fact a single mechanism exists which would explain the several forms of drag reduction that are observed experimentally.

Further, as noted by McNally [45], "it may be said that a contradictory and highly controversial state of affairs exists." One can find contradictory evidence on many aspects of the problem: the nature of the velocity profile in flow is in dispute (Dodge and Metzner [15], Shaver and Merrill [73], Goren and Norbury [26], Seyer and Metzner [71]); the turbulent structure of the flow is changed (Shaver [73], Virk [87]), or virtually unchanged (Goldstein [24], Wells [94]); the axial components of turbulent intensity are changed (Seyer [70]), or unchanged (Goldstein [24]); the transition from a laminar to a turbulent flow regime is delayed (Hershey and Zakin [29], Savins [65], White [100]) or advanced (Ram and Tamir [62], Paterson [55], Goldstein [24]); continuum theory is (Lumley [40]) or is not (McNally [45], Brennen [9]) applicable; etc.

This experiment was designed to study drag reduction by one of the most straight-forward and least controversial means -- by measuring flow rates and pressure gradients in pipes. One of the most effective water-soluble drag-reducing additives known, polyethylene-oxide, was employed, and the concentrations and the molecular-weight species were varied. Because the fluid properties can presumably be altered by preparation techniques and molecular degradation (the reasons commonly advanced for data variance), all

but the most dilute solutions tested in the pipes were characterized by viscosity measurements as well as concentration. Viscosity measurements on samples withdrawn from the flow were made to provide a direct measurement of the degree of molecular degradation. Flow experiments were conducted from below the transition to a highly turbulent regime -- covering a range of two decades in Reynolds numbers and using three pipes with different diameters.

It is hoped that the results of this experimental work will help clarify the behavior of drag-reducing fluid in pipe flow and thereby provide some evidence or clues whereby the drag reduction phenomenon might be better understood.

II. BACKGROUND - A SURVEY OF THE LITERATURE

A. EARLY WORK

One of the first reports of a flow-rate increase due to the presence of additives in a liquid was made by Vanoni in 1946 [86]. He observed that water which contained suspended sand flowed more rapidly than comparable clear water in a laboratory open channel. He attributed the increase to a reduction of the turbulent transfer of momentum due to the sediment, and noted the effect was dependent on both the concentration and the size distribution of the suspended particles.

In the course of the work on the design and testing of flame throwers during World War II, Agoston, Mysels, et al [1] noted anomolous flow behavior for gasoline thickened with Napalm. They attributed the increased flow of the resulting mixture to an apparent decrease in viscosity caused by the "thickening" agent. The paradox of a thickened, jellified liquid offering less resistance to flow than the unthickened solvent was noted by Mysels [53] in 1949, but strangely the phenomenon was not reported in the open literature until 1954 [1].

In 1948 Toms first presented his historic paper [83] observing turbulent-flow friction reduction associated with the presence of polymers in solution. He found that for flow in small diameter tubes, when small quantities of polymethyl methacrylate were dissolved in monochlorobenzene: 1) the pressure gradient required to

maintain a given flow rate for the solution was less than that required for the solvent, 2) the friction reduction was observed in turbulent flow only, not in laminar flow, and 3) the friction reduction was a function of tube diameter and polymer concentration as well as Reynolds number.

In recognition of this landmark work, the phenomenon of friction reduction in pipe flow due to the presence of polymers is now called the "Toms Effect". (Fabula [17] was apparently the first to so entitle the phenomenon.)

With reference to Toms' experiment, Oldroyd [54] postulated that the fluid adjacent to the wall contained a reduced polymer concentration, and thus a viscosity which was less than that of the solution. He interpreted Toms' data in terms of a set of slip-velocity coefficients.

These pioneering reports went relatively unnoticed, and not until 1959 did any further work appear in the literature. Then Shaver and Merrill [73] and Dodge and Metzner [15] published (in the same issue of the Journal of the American Institute of Chemical Engineers) reports on anomolous flow behavior of pseudo-plastic fluids. (The authors referred to their solutions as "dilute", but being on the order of thousands of parts per million, they would be considered as being concentrated by today's standards.) Both Shaver and Dodge used "generalized Reynolds numbers" as flow parameters, and both observed a friction-factor reduction when these non-Newtonian fluids were compared with their Newtonian

solvents. (Non-Newtonian fluids are defined as materials which do not conform to a direct proportionality between shear stress and shear rate.) Their solutions were characterized as power-law fluids with constitutive equations being of the form

$$\tau = K\left(\frac{du}{dr}\right)^n .$$

As well as the pressure gradient and flow rate measurements, Shaver qualitatively studied the nature of the flow by use of dye injection. He made a number of important and far reaching observations, among them:

1) for a given Reynolds number, the polymer solutions had a lower friction factor and a less blunt velocity profile than a Newtonian fluid;

2) the layer of smoothly flowing fluid near the wall was thicker;

3) the Oldroyd suggestion of a slip condition at the wall was invalid for the solutions tested;

4) there was a decrease in the frequency of the vortices generated at the wall; and

5) the radial distribution of "mixing lengths" [67] differed from that obtained for classical Newtonian fluids.

Further, he postulated the existence of a viscosity gradient which increases with distance from the wall. In that his fluids were of the rheological class called "shear thinning", this presumption was natural.

Using a power-law model, Dodge derived a modified form of Prandtl's wall-velocity law. This modification predicted the observed shape of the friction factor vs Reynolds number curves for various values of the power law index, but the agreement between the observed and the predicted values for the friction factor was poor. The model also predicted a more blunt turbulent velocity profile than that in a corresponding Newtonian fluid -- at variance with Shaver's results. Dodge was apparently the first to attribute drag reduction to turbulence suppression brought about by elastic effects in the fluid, although he did not take such effects into account in his model.

Lumley [39] conducted a theoretical analysis and concluded that the Reiner-Rivlin fluid (a purely viscous model of which the simple power-law fluid is a subclass) could not predict the anomolous turbulent-flow behavior. He suggested that the explanation of the phenomenon must, therefore, be sought in viscoelasticity, wherein the strain in the fluid is history dependent.

Several authors have advanced the concept that the elastic properties in viscoelastic fluids provide the mechanism whereby hydrodynamic drag may be reduced. (Metzner and Park [50], Savins [65], Hershey and Zakin [29], Lumley [39].) The basic idea is that the elastic nature of the fluid allows energy to be stored, on some time scale, and this alteration somehow suppresses turbulence, or its growth.

These authors, in general, were influenced by experiments conducted with fluids whose polymer concentrations were in the thousands and tens of thousands of parts per million range, and they thus tended to associate the drag reduction with the rheologically non-Newtonian nature of the fluids. This has led to a problem in semantics which still exists in the field today.

A great impetus to research in the fluid friction reduction phenomenon was provided in the early 1960's when petroleum companies became interested with the prospect of increasing pipe-line capacities and thus cutting the costs of pumping their products [47]. The Western Research Company pioneered in the use of polymers for cost reduction in oil field operations, and in 1960 they introduced the effect to the U.S. Navy. Ram et al [61] have also investigated drag reduction in hydrocarbon solutions.

Probably the reports of Fabula [17], Fabula, Hoyt and Crawford [18], and Hoyt and Fabula [33] in 1963 and 1964 were most instrumental in awakening the interest of many subsequent workers in the field by revealing the startling results that truly dilute solutions of only a few weight parts per million of certain water soluble substances could remarkably reduce hydrodynamic drag in water by as much as 80%. Fabula demonstrated this effect in pipe flow at high Reynolds numbers (on the order of 100,000) for a series of homologous polymers (polyethylene-oxides). Hoyt, Fabula and their coworkers at the Naval Undersea Research and Development Center conducted an extensive study of the effects of additives on fluid friction, using a rotating disk apparatus, pipe flow

experiments, and a "turbulent flow rheometer" [31] which Hoyt developed. They tested a number of polymers, and also showed that drag reduction can be produced by some naturally occurring and living materials, e.g., algae. Their work displayed that the most effective friction-reducing additives have very high molecular weights (greater than 50,000), are linear, unbranched molecules, and are soluble. Another noteworthy contribution of this team was the startling observation that, for concentrations of interest, solutions of one of the most effective drag reducing agents, polyethlene-oxide, are apparently Newtonian!

B. SUBSEQUENT DEVELOPMENTS

1. The Work at M.I.T.

Very noteworthy work in the field has continued at M.I.T. following the early publication of Shaver and Merrill.

Shin [76,49] determined the relationship between intrinsic viscosity and molecular weight for polyethylene-oxide and for polyisobutylene, using light-scattering results as the "calibration standard". He determined the relationship between molecular dimensions and the "critical concentration", i.e. that concentration where the polymer macromolecules would begin to overlap. He studied the drag reduction which occured for aqueous solutions of polyethylene-oxide and for polyisobutylene in cyclohexane with a coaxial cylinder apparatus. Because the more flexible polyethylene-oxide exhibited greater drag-reduction effects than the polyisobutylene for equivalent chain lengths, he concluded that chain flexibility was desirable for optimum drag reduction.

Lee [37] extended the work of Shin, using other polymers in the same apparatus. He found that for equivalent chain lengths, polyacrylamide produced greater drag reduction than polyethylene-oxide. Since the polyacrylamide molecule is less flexible than that of polyethylene oxide, he argued that chain flexibility was not as important as Shin had concluded.

Virk [87], experimenting with solutions of polyethylene-oxide in pipe flow, formulated a hypothesis for the onset of drag reduction, the "Onset Hypothesis". He found that drag reduction occurs only if some critical wall shear stress is exceeded, and the value of this wall shear stress is independent of the solution concentration and of the pipe diameter, and is directly related to the root-mean-square radius of gyration of the unperturbed macromolecule in solution [88,89,90].

Using a light scattering technique, Cottrell et al [12] obtained a direct measurement of the deformation of macromolecules in a solution subjected to a hydrodynamic shear field. They conducted tests on polyisobutylene in decaline. The models of macromolecules in solutions predict that the statistical shape of the macromolecules should change from their unperturbed spherical to an ellipsoidal conformation when subjected to shear. Cottrell found that the degree of deformation was much less than that predicted by models which assume completely flexible or freely-draining coils, and more closely in agreement with a non-freely-draining model which exhibits an internal viscosity. The investigation was

conducted using solutions with concentrations of several hundred parts per million, and it was found that the greatest extension of the major axis was only on the order of 30 percent.

2. The Work at the University of Delaware

Metzner and his colleagues have continued to make worthy contributions to the literature subsequent to his early publication with Dodge.

In 1964 Metzner and Park [50] investigated turbulent flow characteristics of viscoelastic fluids, and also measured some rheological properties. (With the present state of the art, viscoelastic properties can only be seen in concentrated solutions.) They concluded that the observed "turbulence suppression" was related to the ratio of the elastic to the viscous forces developed in the fluid.

Shertzer [75] measured stress functions in concentrated aqueous polyacrylamide solutions over a range of four decades in shear rate -- up to 100,000 per second. The most dilute solution he used had a concentration of 2500 weight parts per million, and in these concentrated solutions, significant normal stress differences were measured.

Seyer [70,71,72] measured velocity profiles and turbulent intensities by photographing small bubbles entrained in polyacrylamide solutions. With Metzner, he analyzed the Townsend-Bakewell [84,4] model for eddies in the vicinity of a wall, and showed how viscoelastic fluid properties could lead to significant

reductions in the production of turbulent energy. This analysis led to a form of similarity law which agrees well with much of the data for velocity profiles near walls and which had previously been deduced empirically [51].

3. Pipe Flow Experiments

a. Velocity Profiles and Turbulent Intensities

Direct measurements of the nature of the flow in pipes have been attempted, but the results have been questionable. The primary reason for the experimental difficulties lies in anomalous fluid properties. Velocity profiles and turbulent intensities are normally measured by use of pitot tubes or hot-wire anemometers. However, due to normal stress differences which exist in elastic liquids, the proper calibration of pitot tubes is difficult. Because these liquids have markedly different heat transfer characteristics, hot-wire probes yield questionable results [77,98]. Astarita and Nicodemo [3] have studied measurements with pitot tubes and hot-wire probes, and have given a good discussion of the experimental problems.

Goren and Norbury [26] found a substantial difference in the velocity profiles between very dilute solutions of polyethylene-oxide (2-5 wppm) and water, the flow being "fuller" (i.e. the velocity gradient near the wall is greater) for the polymer solutions. They also used a polarographic technique [25] using flow samples withdrawn from the flow to determine if the polymer concentration varied radially across the pipe. No variance was found. Squire [80] also reported the turbulent profile to be fuller for the flow of polyethylene-oxide solutions.

Seyer and Metzner [71] reported that the turbulent profile for a 100 wppm solution of a polyacrylamide is "surprisingly flat", and the difference between the profiles of this solution and water can not be discerned on their plot. As mentioned previously, these measurements were made using a photographic technique. Hershey [29] plotted the data of Shaver [73] and found no significant difference between the profiles of the "Newtonian" and the "non-Newtonian" fluids for similar Reynolds numbers.

Turbulent intensity measurements are similarly contradictory. Wells, Harkness, and Meyer [94], using a piezoelectric crystal probe, found that the turbulent intensity measurements in a 500 wppm solution of CMC were the same as those for water and for air. They did find a reduction of turbulent energy in the low-frequency range, and an increase in the high-frequency range for the drag-reducing fluid. Seyer [70] found no change in the radial intensity, but a reduction of approximately 20 percent in axial intensity in their polyacrylimide solutions. Goldstein,[24] using a laser-Doppler instrument, found no significant difference in axial intensities between polyethylene-oxide solutions and water. Spangler [78], using a pitot tube in experiments with polyethylene-oxide and "Polyhall[1]" solutions, found turbulent intensity to be a function of polymer concentration, Reynolds number, and location within the pipe. He found friction reduction in some cases where the turbulent intensity of the polymer solutions was higher than that for water!

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[1] "Polyhall" is the trade name of a commerical anionic copolymer of polyacrylamide and polyacrylic acid manufactured by Stein, Hall and Company.

Carver and Nadolink [11] utilized high speed photomicroscopy to investigate the velocity profile near the wall of a Lucite pipe for water and for various polymer solutions. At a Reynolds number of 4000 they found the laminar sublayer for all additives to be more stable than that for water. The sublayer thickness was greatly increased for the polyethylene-oxide solutions, but for CMC and "Polyhall" solutions, this sublayer thickness showed little deviation from that of distilled water.

In dye-injection studies [23,73] with drag-reducing fluids, it has been observed that a large portion of the small scale, high frequency turbulence is either suppressed or is absent from the flow.

b. Rough Pipes

The results that have thus far been published for experiments in rough pipes are also confusing and seemingly contradictory. McNally [45] tested polyethylene-oxide solutions in a pipe with a roughness factor supposedly large enough to preclude the existence of a laminar sublayer. Since significant friction reduction was observed, McNally concluded that the influence of the macromolecules must extend well beyond the wall layer. Barenblatt, et al [5] conducted similar tests with polyethylene-oxide and polyacrylamide solutions, obtained similar results, and reached the same conclusion.

A. White [96], conducting flow tests in a threaded pipe, found no friction-reduction for guar gum or for aged (seventeen days) polyethylene-oxide solutions, though these same

solutions exhibited friction reduction in smooth pipes! He did observe friction reduction in the threaded pipe for freshly mixed polyethylene-oxide solutions.

Spangler [78] and Brandt, McDonald, and Boyle [8] also conducted flow tests with friction reducing fluids in rough pipes. Spangler used Polyhall while Brandt et al used CMC solutions. Friction reduction was noted in both sets of tests, but the degree of reduction lessened at higher flow rates. These authors attributed the friction reduction to a thickening of the laminar sublayer, and the decrease in effectiveness at higher flow rates to a thinning of the sublayer, thus allowing the roughness elements to protrude through the laminar layer. McNally also observed the decreased effectiveness at higher flow rates, but attributed this to molecular degradation.

c. Miscellaneous Noteworthy Observations

Meyer [51] found he could correlate the results of several experimenters by use of two parameters, the friction velocity,

$$\sqrt{\frac{\tau_w}{\rho}} \quad ,$$

and an empirical parameter which is associated with the polymer and its concentration in solution. These parameters were used to modify the universal velocity profile law, and the resultant form agreed well with the experimental results of several investigators. (As mentioned previously, Seyer and Metzner subsequently arrived at a similarity law of the same form using analytical means).

Meyer observed that the experimental results indicated that the turbulent "mixing length" did not change from that of "Newtonian" fluids. He reasoned, therefore, that the turbulent structure of the flow is essentially uneffected, and that the fluid-friction reduction is due to a thickening of the laminar sublayer. He proposed that the elastic properties of the fluids make the laminar-sublayer less sensitive to disturbance impressed upon it, and therefore the sublayer grows.

F.M. White [99], using Meyers empirical parameters, proposed an "effective Reynolds number" for turbulent pipe flow. Since the pipe friction factor for fluids which obey the Reynolds similarity principle decreases with increasing Reynolds numbers, this idea correlates qualitatively with the drag reduction observed. He also used the thickened sublayer concept to predict the effect of polymer additives on the drag and flow noise for flat plates.

Hershey and Zakin [29] reported the existence of two distinct and different types of drag-reduction in pipe flow. The first type observed only in turbulent flow was characterized by an onset of the effect for fluid velocities greater than some critical velocity. This critical velocity was found to be independent of pipe diameter. (The critical velocity concept differs only slightly from that of a critical wall shear stress.) The second type of drag reduction observed was an extension of the laminar flow regime to higher Reynolds numbers. At higher Reynolds numbers, transition to turbulent flow was observed and no further drag-reduction was noted.

4. Other Drag Reducing Materials

A number of materials have been found that serve as drag-reducing agents in fluids. Sproull [79] observed a significant torque reduction in a rotating-cylinder device when air carried entrained dust particles. Suspensions of wood-pulp fibres in water also display friction reduction in pipes [13]. Certain micellar systems also exhibit this effect [66], as do a number of fibrous and colloidal substances [2,7].

5. Additive - Induced Drag Reduction for Other Geometries

Additive-induced drag reduction has also been observed for the flow of solutions past streamlined bodies [91], flat plates [36], and blunt bodies [63,64,95,97].

It is not known if there is any common mechanism producing all these various forms of drag-reduction.

C. DEGRADATION

The term degradation, as used in this writing, refers to the scission of the molecular chain of a polymer. This scission could be caused by mechanical shearing, chemical reaction, or thermal processes.

The probable existence of molecular scission in turbulent flow has been recognized by nearly all investigators, but the evidence of such degradation has been largely indirect. Normally the lessening of drag-reducing effectiveness which is often observed when polymer solutions age or are subjected to high shear has been attributed to molecular degradation. Conversely, this "effectiveness degradation" has been used as evidence of molecular degradation.

Some investigations of the general problem of polymer degradation have been made by workers in the field of polymer science [46,48,93]. Harrington and Zimm [28] studied the mechanical degradation of polystyrene and DNA molecules in solutions subjected to controlled hydrodynamic shear. The unperturbed random-coil conformation was used in calculating chain tension produced by the shear field. They found that the shear stress necessary to rupture the chains was some two orders of magnitude below that predicted on the basis of bond strengths. Levinthal and Davison [38] criticized the use of the unperturbed coil configuration, and reported results that were based upon a model which assumes that the molecules are in an extended conformation and that the rupture would occur near the chain center. The critical stress so calculated is very close to that estimated from the covalent bond strengths. Levinthal and Davison also stated that several experiments indicated that molecular weights of molecules degraded in controlled hydrodynamic shear were very close to one-half that of the original molecule, though no evidence was given to support this conclusion. (Molecular weight measurements generally cannot be used to determine where breaks occur in the molecular chain. Results of molecular weight measurements using different techniques, e.g. osmometry and viscometry, might be compared to obtain some measure of the molecular weight distributions.)

McGary [44] investigated the degradation of concentrated aqueous polyethylene-oxide solutions, studying the effects of aging, exposure to ultraviolet light, and the presence of oxidizing

and reducing agents in solution. He concluded that polyethylene-oxide degrades ("naturally") primarily by auto-xidation, giving hydroperoxides which decompose by polymer chain cleavage. He also found that the degradation of the polymer in solution was dependent upon the history of the solid polymer resin.

Poreh, Rubin, and Elata [57] measured the drag-reducing effectiveness of a number of polymers as a function of time in an apparatus where the solutions were continuously recycled and pumped through a pipe. It was found, in general, that those additives that produced the greatest drag reduction, (more than a 70 percent reduction) lost their effectiveness most rapidly, but some polymers that produced notable drag reduction (on the order of 45 percent) did not appear to lose their effectiveness.

The only known direct measurement of degradation has recently been made by Paterson [55]. He developed an elaborate viscometer for the measurement of intrinsic viscosities, and made a very fine comprehensive study of the gross flow of polyethylene-oxide solutions in pipes. He withdrew samples from the wall region of the pipes during flow, then by comparing the intrinsic viscosity measurements of these samples with those taken before flow from the solutions being tested, a direct measurement of the degree of molecular degradation was obtained.

D. PROPOSED MECHANISMS FOR DRAG REDUCTION

A number of mechanisms have been proposed to explain the anomalous flow behavior of fluids containing drag-reducing additives. The major schools of thought are represented in the works of Walsh [92], Seyer and Metzner [70,71,72], Fabula et al [19], and Virk et al [87,88,89,90].

It is generally believed that the drag reduction is associated with the viscoelastic properties of the fluids. Walsh and Seyer have proposed specific mechanisms whereby these properties may effect the turbulent structure of the fluid flow.

Walsh envisions the polymer molecules interacting with small scale disturbances in the viscous sublayer near a wall. The macromolecules are thought to extract energy from the disturbances by being deformed in the interaction, thus damping the small scale disturbances. The disturbances that are thus damped would, if the polymer molecules were not present, grow by extracting energy from the velocity profile near the wall.

Seyer and Metzner have analyzed the so-called Townsend-Bakewell model. In this model, large eddies are assumed to exist in Newtonian flow as counter-rotating pairs within the wall region with their axes of rotation parallel to the flow. The fluid passing between the counter-rotating eddies is elongated or stretched. Any elasticity of a fluid would make this stretching more difficult, thereby reducing the radial momentum transfer rates, and thus reducing the turbulent flow drag. Seyer's analysis impressively yields similarity laws for drag-reducing fluids that has previously been deduced empirically.

Fabula et al have proposed a molecular entanglement hypothesis wherein polymer macromolecules are clustered in turbulent shear flow. The entangled macromolecules stretch into fibers in shear flow. This fibrous network might interfere with the turbulent structure of the flow. The migration of the entanglements away from intense shear layers is also suggested as a possible means whereby locally intense shear layers might be diffused, thus reducing the intensity of local disturbances.

Though qualitatively appealing, these mechanisms have not yet been subject to experimental verification. The viscoelastic properties of dilute solutions are, at best, difficult to measure. One of these properties, which can be measured for concentrations of drag-reducing interest is the normal-stress difference. It has been reported [5,9] that while measureable normal-stress differences disappeared after the solutions were aged for several days, significant drag reduction remained. (Of course, elasticity may exist on a microscopic scale even though its effects are not observed macroscopically.)

Though no specific mechanism has been proposed, one of the most significant contributions yet made in the field has been Virk's recognition of the existence of a critical wall shear stress in the flow of polymer solutions. According to Virk's "Onset Hypothesis", drag reduction will occur in the turbulent flow of polymer solutions if, and only if, the wall shear stress exceeds some minimum value. The value of the wall shear stress is hypothesized to be related only to the size of the macromolecules

in solution. Specifically, the critical wall shear stress varies inversely with the square of the r.m.s. radius of gyration. This hypothesis also predicts that the onset of drag reduction should be independent of the polymer concentration. While a relatively slight concentration dependence has been observed for the critical wall shear stress [23a,55], the existence of such a critical stress and its importance as a dominant parameter have been verified by many investigators.

III. THE POLYMER IN DILUTE SOLUTION

A. GENERAL

The character of macromolecules in solution has been the object of extensive study during the past two decades. With the powerful tools of statistical mechanics and the insights of chemistry, physical chemists, chemical physicists, and rheologists have developed models which apparently well describe macromolecules in solution.

The geometric picture that emerges from these statistical models for very large linear molecules in dilute solutions is that of flexible chains randomly coiled into spherical shapes. The coiling is caused by Brownian motion, and the dimension of the sphere depends upon the specific polymer, the solvent, the chain length, and the temperature.

The composition of the molecular chain is, of course, the dominant influence upon the conformation of the macromolecule. Preferred energy considerations dictate the relative orientation of successive segments as well as the bonding angle between segments. The nature of the bonds may allow considerable flexibility, or may require considerable rigidity in the molecular chain.

The interaction between the segments of a macromolecule and the molecules of the solvent also influences the conformation. If the relative affinity between segments of the macromolecule and the surrounding solvent is great, as in the case of a good solvent,

the chain will tend to spread out and thus the random-coil sphere will be larger. On the other hand, if the relative affinity between chain segments is much greater than that between segments and the solvent molecules, as in the case of a poor solvent, the sphere will be correspondingly smaller. The solvent wherein the chain would form its tightest conformation is called the "theta-solvent". This conformation is also called the "unperturbed" conformation.

The size of a random coil is often characterized by the root-mean-square end-to-end distance $\langle r^2 \rangle^{\frac{1}{2}}$ of the polymer chain. Another related measure is the root-mean-square radius of gyration $\langle r_g^2 \rangle^{\frac{1}{2}}$, which is related to the r.m.s. end-to-end distance for flexible molecules by $\langle r^2 \rangle = 6\langle r_g^2 \rangle$ [21].

The principal methods currently used for experimentally determining the dimensions of macromolecules in dilute solutions are light scattering and intrinsic viscosity measurements. The light scattering technique is a more direct method , but it is fraught with a number of experimental difficulties. On the other hand, experimental data of high precision may be obtained with viscosity measurements, but the interpretation of these data in terms of molecular dimensions or weight requires a prior calibration against a primary method, e.g. light scattering or osmometry.

B. INTRINSIC VISCOSITY

The macroscopic viscosity of a solvent having large, suspended particles, even in dilute concentrations, as determined by any measuring device, is different from that of the pure solvent. This

arises from the fact that the particles will cause perturbations in the normal solvent flow pattern, thus increasing the rate of energy dissipation. This change in viscosity can then be used to measure the size of the suspended particles.

Einstein [16] first calculated the change in viscosity due to very dilute concentrations of rigid spheres in suspension. He found

$$\eta = \eta_o(1 + 2.5\phi) \tag{3-1}$$

or

$$\eta_{sp} = \frac{\eta}{\eta_o} - 1 = 2.5\phi,$$

where

η = the shear viscosity of the solution

η_o = the shear viscosity of the solvent

ϕ = the volume fraction occupied by the spheres

η_{sp} = the specific viscosity of the solution.

The striking aspect of this result is the fact that the change in viscosity does not depend on the size of the individual suspended particles, but only on the total volume occupied by the particles! This result is valid as long as the interactions between spheres is negligible.

Guth and Simha [27] extended Einstein's treatment to asymmetric particles, with the result that the viscosity of a solution containing such particles depends on their orientation. If ellipsoidal particles are oriented with their long axes parallel to the streamlines of flow, the viscoisty is lower than if such particles were randomly oriented.

The specific viscosity shows the incremental viscosity attributable to the solute, and the ratio η_{sp}/c is a measure of the capacity of the solute to increase the viscosity of the solution. The limiting value of this ratio at infinite dilution is designated the intrinsic viscosity, $[\eta]$. Thus,

$$[\eta] \equiv \lim_{c \to o} \left(\frac{\eta_{sp}}{c} \right) = \lim_{c \to o} \left(\frac{\eta}{\eta_o} - 1 \right) . \qquad (3\text{-}2)$$

For intrinsic viscosity purposes the concentration c is customarily expressed in grams of solute per 100 milliliters of solution.

Huggins [34] proposed the following equation for determining the intrinsic viscosity of a polymer:

$$\frac{\eta_{sp}}{c} = [\eta] + k'[\eta]^2 \, c . \qquad (3\text{-}3)$$

The relative viscosity of the polymeric solution is measured at several concentrations, and $\frac{\eta_{sp}}{c}$ vs c is extrapolated to zero concentration to obtain $[\eta]$. (For some molecules, the value of $[\eta]$ depends upon the shear rate of the viscosity measurements. In this case, several different low shear rates should be used, and these results extrapolated to zero shear.)

As can be seen from the development, $[\eta]$ is related to the volume occupied by a molecular coil. There has been no adequate theoretical treatment of the constant k' in Huggins equation, but in general its value is thought to be determined by hydrodynamic interactions between molecules and by the effect on these

interactions caused by molecular shape and flexibility [52]. Its value is approximately constant for a series of polymer homologs, normally in the range of 0.35 - 0.40.

A number of other equations exist which may be used for the determination of the intrinsic viscosity [20,35,43,82]. Several schemes have been developed which use a single viscosity measurement [42,68,69], and it is argued that these are generally as accurate as those requiring a series of measurements and extrapolation due to the introduction of experimental error in changing concentrations.

A vast amount of experimental verification has shown that the intrinsic viscosity is related to the viscosity-average molecular weight $\bar{M}_v$ by the equation

$$[\eta] = k \bar{M}_v^a \quad . \tag{3-4}$$

Equation (4) is called the Mark-Houwink equation, or the modified Staudinger equation. ($[\eta]$ is sometimes called the Staudinger index, as Staudinger first proposed using viscosity measurements to characterize polymer solutions.)

k and a are experimentally determined constants which are independent of molecular weight, but are dependent on the nature of the polymer, the solvent, and the temperature. For a theta solvent, a has a value of 0.5. In good solvents, a is normally in the range 0.65 - 0.85 for molecules that have a flexible-coil conformation [52].

Flory [20] also shows that the exponent relates the viscosity average to the most probable "number" and "weight" average molecular weight distributions as follows,

$$\bar{M}_n : \bar{M}_v : \bar{M}_w :: 1 : [(1+a)\Gamma(1+a)]^{1/a} : 2 \qquad (3\text{-}5)$$

where

$\bar{M}_n$ = Number average molecular weight = $\sum_i N_i M_i / \sum_i N_i$

$\bar{M}_w$ = Weight average molecular weight $\sum_i N_i M_i^2 / \sum_i N_i M_i$

N_i = Number of molecules with molecular weight M_i, and

$\Gamma(1+a)$ = Gamma function of $(1+a)$.

Thus the viscosity-average molecular weight is very close to the weight-average for most large molecules.

According to Flory, the viscosity method is fundamentally rooted upon the relationship

$$[\eta] = \Phi \langle r^2 \rangle^{3/2} / M. \qquad (3\text{-}6)$$

This relationship has been confirmed for a great many randomly coiled polymers. Φ is a constant reasoned to be the same for all polymers. Its experimentally determined value is $2.5 \pm 0.1 \times 10^{21}$, and recent theory [21] places its value at 2.66×10^{21}.

C. THE EQUIVALENT HYDRODYNAMIC SPHERE

A convenient representation for a flexible polymer in solution is that of a rigid sphere. If the molecules of a solvent are assumed to be entrapped within the coils of the polymer, so that

the solvent-solute ball moves essentially as a unit, the rigid sphere representation is quite plausible. Another representation, the freely-draining coil, envisions that the solvent molecules pass freely through the polymer without hinderance. Experimental evidence favors a non-freely-draining model.

The equivalent solid-sphere representation may be obtained from either thermodynamic considerations for the "excluded volume" of flexible polymers, or from hydrodynamic considerations based on the frictional resistance to flow of the solvent-solute ball outlined above. Tanford covers both approaches in his reference book [81].

The effective diameter of the polymer sphere can be related to the r.m.s. end-to-end distance of the polymer by

$$D_{eff} = \gamma \langle r^2 \rangle^{\frac{1}{2}} . \qquad (3\text{-}7)$$

It remains, of course, to calculate γ for each polymer-solvent in question. This is normally accomplished using the so called Kirkwood-Riseman model for the molecule, wherein the polymer chain is represented as a connected chain of spherical beads with bond lengths and bond angles considered as in the calculation of the dimensions of the polymer. The Stokes-flow frictional coefficient is calculated with this model, and the coefficient γ is obtained when substituting D_{eff} for $\langle r^2 \rangle^{\frac{1}{2}}$.

D. POLYETHYLENE-OXIDE IN WATER

1. Polyetheylene-Oxide

The polymer of specific interest in this work is polyethylene-oxide. This linear, long-chain, water-soluble polymer is one of the most effective drag-reducing additives known. Its chemical structure is represented by $(-CH_2-CH_2-O-)_n$, n being the number of repeating units, or mers. The maximum length of one unit is about 3.6Å, and the maximum cross-sectional diameter is about 2.9Å [59]. From the basic mer with a molecular weight of 44, this molecule can be commercially polymerized to molecular weights of several million.

Mark and Flory [41] have analyzed the configuration of the polyethylene-oxide chain, and found that the conformation of lowest energy consists of a succession of trans-gauche-trans configurations of the bonds. Beech and Booth [6] measured the intrinsic viscosity of polyethylene-oxide using various solvents, and their results support the calculations of Flory.

2. Water Solubility

The polyethylene-oxide molecules have such an affinity for water (through hydrogen bonding) that the resin surfaces begin absorbing the water upon contact. This results in cohesion at the resin-water interface, and large particles may agglomerate if care is not exercised in mixing. Agglomerations are most easily avoided by first mixing a slurry of the resin and some suitable dispersing agent, such as polyglycol or isopropanol. This slurry can then be easily mixed with water.

3. Molecular Weight Distribution

The polymer resin may be obtained from the Union Carbide Chemical Company in eight commerical grades with average molecular weights ranging from 100,000 to nearly 10,000,000 [85]. This company produces two series of the PEO polymer, designated as WSR or WSR N. The WSR series possesses a greater thickening power for the same average molecular weight. The WSR N series has a narrower molecular weight distribution, supposedly because it does not possess nearly as much of a high molecular weight tail as that of the WSR series.

Due to the difficulty of fractionating this polymer without altering its degree of polymerization, the molecular weight distributions are not well known. According to Powell and Bailey [58], the molecular weight distribution of PEO is "narrow". However, in some gel permeation chromatography measurements [55], a WSR-205 blend appeared to possess a very broad distribution with the ratio of weight average to number average molecular weight being on the order of twenty. Because the gel permeation technique tends to degrade the polymer these results are suspect.

(In gel permeation chromatrography, a solution containing the polymer is passed through a column of gel. The gel allows the various macromolecules to pass at different rates depending upon their size. Refractive indices of the effluent are continuously measured, and the differential refractive index (between the solution and the solvent) is a measure of the product of the number of molecules and their molecular weight contained in the effluent at that time.)

Commerical grades of PEO are specified as producing a solution viscosity in water within some limits at some (high) concentration. For example, the specifications for WSR-301 require a one percent (10,000 wppm) aqueous solution at a temperature of 25 C. to have a viscosity of 1500 to 3500 centipoises [85]. Resins are blended to achieve this specification, so it is not surprising that some difference exists between blends of the same commerical grade of the polymer.

4. The Mark-Houwink Relationship and the Critical Concentration

Shin [76] conducted light scattering and intrinsic viscosity determinations for polyethylene-oxide in water, and found the Mark-Houwink relation for this polymer at 25 C. to be

$$[\eta] = 1.03 \times 10^{-4} \bar{M}_v^{0.78}. \qquad (3\text{-}8)$$

(Bailey [58] previously reported the relationship at 30 C. to be

$$[\eta] = 1.25 \times 10^{-4} \bar{M}_v^{0.78} . \qquad (3\text{-}9)$$

The temperature difference does not account for this variance, so it is assumed that the difference in the measurement of the coefficient lies in experimental uncertainty.)

As a further noteworthy contribution, Shin determined the proportionality coefficient for the hydrodynamically equivalent sphere. According to his calculation,

$$\gamma^2 = 0.784 + 0.0312 \ln [\eta]. \qquad (3\text{-}10)$$

Based upon the effective volume of the equivalent hydrodynamic sphere, Shin then determined the critical concentration C_c, for macromolecular overlapping to be

$$C_c = 4.93 \times 10^{-3} \frac{1}{\gamma^3} \frac{1}{[\eta]} \quad . \qquad (3\text{-}11)$$

From Shin's plot of this equation, this author has approximated the critical concentration for PEO in water to be

$$C_c' = 7.2 \times 10^3 [\eta]^{-1.07} \quad , \qquad (3\text{-}12)$$

with C_c' given in weight parts per million (wppm). This equation gives values for the critical concentration within two percent of the values obtained from equation (3-11).

5. The Effect of Shear on the Intrinsic Viscosity of Polyethylene-Oxide

According to Peterlin [56], freely flexible linear molecules in solution should exhibit a marked shear thinning effect, i.e., the measured viscosity should be lower for higher shear rates. This would result from the macromolecules being elongated and aligned with the stream lines in flow.

The greatest portion of experimental evidence indicates, however, that shear thinning does not occur in dilute aqueous polyethylene-oxide solutions. Hoyt [31], Shin [76], Virk [87], and Booth [6] have all reported that they have observed no significant change in viscosity with shear for polyethylene-oxide. (This author has also found an absence of shear dependence over a five-fold range of shear rates.)

Paterson [55], however, in a specially constructed, high-precision, low-shear capillary viscometer did observe a marked increase in the viscosity of WSR-301 at low shear rates, even in dilute solutions.

Thus, as with so many other aspects of the drag-reducing additive problem, the evidence concerning the effect of shear on the intrinsic viscosity is contradictory.

IV. THE PIPE FLOW EXPERIMENT

A. EXPERIMENTAL SET-UP

The basic pipe flow facility used in this experiment consisted of a 75-gallon stainless-steel pressure tank which served as a reservoir, a two-inch diameter intermediary section equipped with two-inch ball valves, three test pipes having different diameters with corresponding conical entrance adaptors, and various pressure transducers. The experimental set-up is shown schematically in Fig. 1.

The desired flow rates were obtained by either varying the hydrostatic head in the reservoir or, for large rates, pressurizing the reservoir with either compressed air or bottled nitrogen. The flow rates were determined from the weight of efflux caught in a measured time.

The entrance adaptors of the test pipes were relatively short and conical in shape. The purpose of this geometry was to achieve a desired compromise in the entry flow. The conical shape serves to smooth the flow and reduce the sharp inlet contraction and corresponding large energy losses which occur at abrupt transitions. On the other hand, it was desired to achieve transition to turbulent flow close to the entrance of the pipe. Thus, the conical sections were made relatively short with a small ridge at the pipe entrance to perturb the flow slightly, thereby promoting transition.

The overall dimensions of the test pipes were as follows: (diameter x length); 0.249 in. x 17.0 ft; 0.394 in. x 24.0 ft; 0.775 in. x 29.25 ft. The test pipes were of commerical stainless steel tubing, and no polishing or other treatment was used to achieve special smoothness.

The pipes were tapped at various stations positioned as shown in Fig. 2. Each station was tapped with a 10-32 thread, and the hole was carefully deburred. This station could then accommodate either the sample extractor (Fig. 3) or the pressure transducer adaptors. The adaptors were carefully machined so that when they were tightened, the adaptor inner face was flush with the inner edge of the pipe. The pressure tap hole was 0.0635 in. in diameter. This conforms to Shaw's criterion for obtaining accurate static pressure measurements for flow experiments [74].

The pipe wall-pressure was obtained by means of either a Statham Model PG769 pressure transducer or a Statham Model UC-3 Universal Transducing Cell with pressure accessories. The latter type of transducer has interchangeable diaphragms for the pressure accessory. This feature proved most useful since an appropriate diaphragm could be selected to achieve the best possible signal to noise ratio and thus optimum accuracy for the flow conditions prevailing during a series of runs. Diaphragms ranging from maximum pressure ratings of 1 psi to 100 psi were used. Both the Model PG 769 and Model UC-3 are strain-gage transducers.

The analog readouts for these transducers were obtained through the use of Statham Models UR-4 and UR-5 Universal Transducer Readouts, or through four battery-powered units constructed for this experiment. Hewlett-Packard Moseley Models 7035B and 2DR-2A X-Y recorders and a Clevite Brush Model Mark 220 Dual Channel Strip-Chart Recorder were used to obtain pressure-versus-time recordings for each run.

A Heise Model CMM bourdon-tube gauge was attached to the two-inch intermediary pipe near the entrance of the conical entrance adaptor. This pressure gauge has a specified accuracy of 0.1 percent of its full scale reading (200 psig), a specified reproductibility of 0.02 percent full scale, and is rated as a secondary calibration standard. Thus, it was used both to calibrate the strain-gage transducers and to measure the pressure at the pipe entrance.

B. EXPERIMENTAL PROCEDURES

1. Preparation and Handling of Solutions

Several investigators have reported difficulty in obtaining reproducible data in drag-reduction experiments, and normally they attribute this to faulty mixing procedures or to polymer degradation. In order to minimize such problems, a standard mixing and test procedure was adopted. In addition, all but the most dilute polymer solutions were characterized by viscosity measurements.

In order to facilitate mixing the polyethylene-oxide resin with water, the resin was first dispersed in polypropylene-glycol, (a product marketed by the Dow Chemical Company as POLYGLYCOL P400). Since polyethylene-oxide is insoluble in polyglycol, the granules of the resin are held in suspension, well separated and ready to mix with water. The appropriate amount of resin to achieve a desired concentration in the final solution was mixed with 250 milliliters of polyglycol. This slurry was then added to 90 kilograms of tap water, and the resulting solution was gently mixed with a mechanical stirrer for twenty minutes. (The mixing was accomplished in 32-gallon polyethylene garbage cans. A test mix normally consisted of 270 kilograms of solution, using three cans. After allowing the solutions to age for about twelve hours, the mixes were again stirred for a couple of minutes. Experiments were conducted within twelve to twenty-four hours of the original mixing.

(The polyglycol has a molecular weight of approximately 400. Viscometery tests were conducted and they confirmed that no measurable difference in intrinsic viscosities existed between solutions mixed with and without the dispersing agent for the proportions used in this work.)

The reasoning behind the twelve-hour aging period and subsequent stirring is as follows: Intrinsic viscosity measurements were made on several solutions during the aging process. It was found that within four to six hours after mixing, there was a

significant reduction in intrinsic viscosity for WSR-301 solutions, e.g., ca. 15-16 to 12-13. After this period, the viscosity would remain approximately constant for several days. It is thought that the initial high viscosity may be due to molecular entanglements and/or incomplete solvation of the resin. The aging period allows more time for the material to go into solution, and for the solute macromolecules to disentangle.

The solutions were transferred to the pressure tank through a 5/8 inch ID flexible hose. A slight suction was used to transfer the solutions from the garbage cans in a gentle manner to minimize degradation. Samples were withdrawn from the tank at the time of the flow tests. The viscosities of these samples were normally measured within six hours. The samples were stored in a refrigerator to minimize degradation.

2. Transducer Calibration and Flow Measurements

To calibrate the transducers, the test pipe was filled with water, the exit end was capped, and the transducers were calibrated *in situ*. Compressed air or bottled nitrogen was bled into the tank until the maximum desired pressure was achieved. Calibration points were taken at various pressures as gas was bled from the tank. (It was found that hysteresis sometimes occurred if calibration points were taken initially in the "upward" direction. This is an effect of the bourdon tube, and no hysteresis was noted if the Heise gauge was subjected to the maximum pressure desired before calibration.) Either X-Y or strip chart recorders were used to record the various pressures during the test runs.

Tap-water flow tests were used to check the accuracy of the system. Tap-water runs were made extensively before any polymer solutions were tested, and then occasionally between polymer batches to check for any change in the characteristics of the pipe, e.g. corrosion. The pressure readings taken at the various stations during water flow also served as a check on the smoothness of the pressure taps. (The initial pressure readings taken during water flow tests at two stations in the 0.249-inch pipe and at one station in the 0.394-inch pipe did not fall on the predicted linear gradient. Close inspection revealed tiny burrs at these stations. When these burrs were removed, the subsequent pressure readings did fall on the linear gradient.) As an indication of the accuracy of the system, the pipe-friction factors obtained in the water flow were consistently within three percent of the Prandtl curve for turbulent flow of a normal liquid in smooth pipes [67].

The pressure gradients measured were based on the output of from three to five transducers. Excellent linearity was observed throughout the tests. The accuracy of the pressure gradient measurements was on the order of one percent. (The gradient was determined using a least-squared-error fit to the data. The calculations were made using a Hewlett-Packard Model 9100A Desk Calculator and a standard library program.)

The procedure followed during an actual flow test was as follows. The reservoir was pressurized to a desired level, and then the ball valve at the pipe entrance was opened. The valve

controlling the appropriate pressure source, i.e., the compressed air or the bottled nitrogen, was manually adjusted until a desired constant entrance pressure was maintained as indicated on the Heise gauge. The entrance pressure was continuously monitored and held constant while the flow rate was being measured.

Flow rates were determined to an accuracy of 0.75 percent by the catch, time, and weigh technique. The pipes ended abruptly at their exits without valves or other extraneously perturbing influences, though short lengths of flexible hoses were used to facilitate catching the flow at the higher flow rates.

A number of weighing devices were employed during this experiment. The polymer resin used to mix a given concentration of solution were weighed on either a Mettler Model H15 Precision Balance, (accurate to 0.001 gram,) or a Welch Lab Balance (to 0.01 gm.). For the flow rate determinations, weighing was accomplished on either a 0-500 lb. Toledo scale (to $\pm$ 0.25 lb.), a 0-100 lb. Fairbanks-Morse scale (to $\pm$ 0.1 lb.), or a Cenco Laboratory Balance (to $\pm$ 0.1 gm.). Flow times were obtained using a stopwatch (to $\pm$ 0.1 sec.).

The ambient temperature during the tests ranged from 22.5 to 25.0 Celcius.

C. RESULTS

1. Preliminary Discussion

The resistance to flow in a pipe is normally represented by the pipe friction factor, λ. This coefficient is defined by

the equation

$$\lambda = \frac{\frac{dP}{dL}\, d}{\frac{1}{2}\rho U^2}, \qquad (4\text{-}1)$$

where

dP/dL = pressure gradient,

d = pipe diameter,

ρ = density of the fluid, and

U = mean flow velocity.

The mean flow velocity is equal to the volume flow rate, Q, divided by the cross-sectional area of the pipe, A.

The wall shear stress, τ_w, is determined from

$$\tau_w = \frac{dP}{dL}\,\frac{d}{4}. \qquad (4\text{-}2)$$

This expression is determined from a balance of forces and is independent of the nature of the fluid. For the laminar flow of a normal fluid in a circular pipe (Poiseuille flow), the Navier-Stokes equations can be used to show that

$$\lambda = 64/N_R, \qquad (4\text{-}3)$$

where

N_R = pipe Reynolds number = $\frac{\rho U d}{\eta}$, and

η = coefficient of viscosity.

The laminar regime normally exists up to a Reynolds number on the order of 2000. This value can be greatly increased if extreme care is exercised in obtaining smooth entrance conditions. At

the higher end of the laminar region, experimental results usually depart from the Poiseuille law with slightly higher friction factors observed than predicted. The reason for this is still being debated. This region is sometimes called the "unsteady laminar" flow region. There then occurs a range wherein the flow characteristics are "intermittent", i.e., there are alternate patches of laminar flow and turbulence in the pipe. In this Reynolds number region, the character of the flow undergoes "transition" from a laminar to a turbulent regime with a corresponding large increase in λ. The flow is described as "fully turbulent" when no laminar patches remain. In the fully turbulent regime, normal fluids obey the semi-empirical Prandtl "universal law of friction for smooth pipes" [67],

$$\frac{1}{\sqrt{\lambda}} = 2.0 \log (N_R \sqrt{\lambda}) - 0.8 . \qquad (4\text{-}4)$$

In this paper, the percent drag-reduction is defined as

$$\text{Percent drag-reduction} = (1 - \frac{\lambda}{\lambda_o})100, \qquad (4\text{-}5)$$

where

λ = the pipe friction factor for the solution tested, and

λ_o = the pipe friction factor for the solvent at the same Reynolds number.

When a fluid enters a pipe, the velocity profile is initially nearly uniform. As the fluid progresses downstream, the velocity distribution changes due to friction at the wall. At

some distance from the entrance a fully developed profile is achieved, and is unchanged from that point as the flow proceeds downstream. This distance is called the entry or inlet length.

According to Schlichting [67], the entry length for laminar flow is on the order of 150 to 300 pipe diameters. For turbulent flow, he states that this length is normally less than 50 diameters. In laminar flow, the velocity profile is parabolic. In turbulent flow, the velocity gradient at the wall is greater and, because of turbulent mixing, the velocity is nearly uniform. The shape of the velocity profile for turbulent flow may be described qualitatively as a blunted parabola.

The energy loss per unit length is greater near the entrance, and this is reflected in higher pressure gradients in this region. Beyond this entry length, constant, linear pressure gradients indicate that the character of the flow is not changing in the axial direction [30].

Thus, from determining the flow rate and pressures along a pipe, it is possible to discern information concerning the nature of the flow in addition to obtaining the pipe friction factors.

In this work, most of the flow tests were conducted using the ¼-inch pipe, primarily because the lower flow rates were much more manageable, and more data could be obtained from a given polymer mix.

In keeping with the usual practice for dilute polymer solutions, the Reynolds numbers determined in this work were calculated using the viscosity of the solvent, i.e., water.

2. Friction Reduction as a Function of Polymer Concentration

The results of a number of flow tests conducted in the ¼-inch pipe to determine the effect of polymer concentration on pipe friction are summarized in Fig. 4. In these tests, the polymer resin was WSR-301, blend 3213. The viscosity measurements for this blend in the solutions tested yielded a mean intrinsic viscosity of 12.9, which corresponds to a molecular weight of 3.4×10^6.

The following tabulation shows the percent drag-reduction obtained for various concentrations of WSR-301 at a Reynolds number of 30,000.

Concentration, wppm	Percent Drag Reduction
1	44
3	57
7.5	70
10	74
25	74
50	74
100	74

It can be seen that the percent drag reduction per unit concentration decreases with increasing concentrations. For these flow conditions, the maximum percent drag-reduction is attained at 10 wppm. Beyond this concentration, a saturation effect appears to exist. There is no discernible difference in the friction factors for 25, 50, and 100 wppm.

For the more dilute solutions, i.e. 10 wppm and less, it is observed that the friction factors increase for Reynolds number above N_R = 30,000. This lessening of drag-reducing effectiveness is probably due to degradation. The degradation measurements taken during this work (Chapter 5) tend to support this conclusion.

3. Transition

In Fig. 4, the marked increase in the pipe friction factors in the Reynolds number range of 5000 - 6000 indicates the occurrence of a transition to a turbulent flow regime. The rise in the friction factor for the 1, 3, and 7.5 wppm WSR-301 solutions can be correlated with pressure fluctuations observed on the transducer outputs (Figs. 5-8.). The fluctuating flow is characteristic of intermittency, or the existence of both turbulent and laminar patches in the flow.

No transition or intermittency was noted for the 50 wppm WSR-301 solutions in the ¼-inch pipe. (Having observed no evidence of intermittency at a number of set flow rates, the flow range of interest was slowly swept by varying the pressure in the tank, and the transducer outputs were continuously monitored. No discernible change in the flow characteristics was evidenced.) However, it is noted that a transition was observed for the 50 wppm solutions in the 0.394-inch pipe (Fig. 9.). This observation is discussed in the succeeding section.

Viewing the friction-factor plot in Fig. 4 and the transducer outputs recorded in the transition region (Figs. 5-8), the

following observations are made:

1. The Reynolds number corresponding to the onset of intermittency decreases with increasing polymer concentration.

2. The Reynolds number range over which intermittency occurs decreases with increasing polymer concentration.

3. The magnitude of the pressure fluctuations appear to be independent of polymer concentration.

4. The generally lower friction factors observed with increased polymer conentration in the region immediately before transition indicate that the polymer does have some stabilizing effect on the flow.

4. The Effect of Pipe Diameter

In order to see if any "diameter effect" exists, flow experiments were conducted with solutions of 50 wppm WSR-301 in the three test pipes. The results are shown in Fig. 9.

At Reynolds numbers above 40,000, no significant difference is noted in friction factors of the various pipes. However, the transition characteristics are markedly changed. Whereas no transition was observed for the 50 wppm solutions in the $\frac{1}{4}$-inch pipe, an abrupt increase in friction factor and transducer output-pressure fluctuations evidenced intermittent flow and transition for the 0.394-inch pipe.

The transitional flow region for the 3/4-inch pipe could not be tested without modifying the apparatus. However, Paterson's plot of the friction factor versus Reynolds number for a 50 wppm

WSR-301 solution in a 3/4-inch pipe shows the polymer curve (no data is shown) breaking away from the Prandtl curve above a Reynolds number of 3600. Thus, the evidence indicates that transition would occur in the 3/4-inch pipe, and that normal (Prandtl curve) turbulence would be observed before the onset of drag reduction.

The seeming diameter-effect anomaly in the transition region is actually further evidence to support Virk's Onset Hypothesis. (According to Virk, the onset of drag reduction occurs when the wall shear stress exceeds some specific value.) If the critical wall shear stress is exceeded at a Reynolds number below that at which transition would normally occur, then there is no marked transition. This situation obtains for 50 wppm solution in the 1/4-inch pipe. On the other hand, if the wall shear stress is less than critical in the transition region, as occurs in the larger pipes, (and for the more dilute concentrations in the $\frac{1}{4}$-inch pipe,) intermittency and transition would occur. When the critical shear stress is reached, then drag-reduction begins.

In Virk's hypothesis, the critical wall shear stress is independent of concentration, and depends only on the size of the macromolecule. However, the increase in transition Reynolds number with decreasing concentration seen in this work indicates that the critical wall shear stress decreases with increasing concentration. This is in accord with Paterson's observation. Also, Gadd [23a] reported the critical wall shear stress for WSR-301 decreased from 6.5 dyne/cm^2 for a 2 wppm solution to 1.5 dyne/cm^2 for a 35 wppm solution.

5. Entrance Effects

The effect of drag-reducing additives on pipe entry length is not known. Seyer and Metzner [71] speculate that this distance should be significantly increased for drag-reducing systems, but the only known previous measurements (taken by Dodge and Metzner [15]) indicate no appreciable increase in this entry length.

In this experiment, the first test stations for the various pipes were located at 150, 122, and 93 diameters from the entrance for the 0.249, 0.394, and 0.775 inch pipes respectively. The pressure gradient measurements indicate that these stations were not in the entry length. (Had the first stations been within the entry length, the pressure readings at that station would have been relatively higher than the rest of the stations due to the excess pressure drop that occurs in the entry region. The pressure measured at this station fell consistently on the linear gradient established from measurements taken further downstream.)

No known investigation of the relative pipe-entrance losses for polymer solutions had been conducted. Pruitt and Crawford [59] have reported an "end-effect" in capillary flow. They found, in the course of rheological studies, that more energy was required to force polymer solutions into small tubes than was required for the associated solvents.

In the course of this experiment, it was initially thought that the entrance losses for the polyethylene-oxide solutions were very much greater than those for water. For

example, the pressure dropped from 85.0 psig at the ¼-inch pipe inlet to 48.5 psig at the first station for a 50 wppm WSR-301 solution. The drop for water was from 85.0 to 64.4 psig. Upon further thought it became apparent that this pressure drop between the entrance and the first station was not a valid indication of entrance losses since the flow rates were not comparable. (The flow rates attained for the polymer solutions were nearly twice as large as those for water at the same entrance pressure.) However, the relative pressure drops observed for comparable Reynolds numbers also indicated greater entrance losses with the polymer solutions.

To obtain a better measure of the relative losses for the various solutions, the following technique was employed. The difference between the inlet pressure (as measured by the Heise gauge) and the zero-length pressure (obtained by extrapolating the established pressure gradient back to the entrance) was compared at comparable Reynolds numbers. It was found that the entrance losses, measured in this manner, generally increased with polymer concentration.

To illustrate this observation, the following tabulation shows this pressure difference for various concentrations of WSR-301 for Reynolds numbers of about 50,000.

Solution	$P_o - P_o'$ (psi)	Reynolds Number
Water	3.6	50,000
1 wppm	3.4	50,000
3 wppm	3.9	48,700
7.5 wppm	4.6	47,300
25 wppm	7.3	54,000
50 wppm	6.5	51,000
100 wppm	6.5	47,500

P_o = Inlet pressure indicated on Heise Gauge

P_o' = Extrapolated zero-length pressure

V. DEGRADATION IN PIPE FLOW

A. OBJECT OF THE DEGRADATION MEASUREMENTS

Prior to the recent work of Paterson [55], no known experiments had been conducted to measure directly the degree of molecular degradation which occurs in the turbulent pipe flow of polyethylene-oxide solutions. The indirect evidence of degradation, i.e., the lessening of drag-reducing effectiveness which has been observed after polymer solutions have been subjected to turbulent flow in pipes, has left unanswered some pertinent questions. For example:

1. Is the lessening effectiveness actually caused by molecular scission?

2. From the indirect evidence, the degradation appears to occur in turbulent flow regimes -- the same regimes wherein the drag-reduction phenomenon occurs. Could the drag-reduction be an effect caused by the molecular degradation?

3. What is the nature of the degradation that occurs in pipe flow? Is it mechanical in nature, or could it be caused by chemical reactions? If the degradation is caused primarily by some chemical process, perhaps such reactions could be inhibited by suitable additives.

Thus, the object of this portion of the experiment was to obtain a direct measurement of the amount of degradation, and to attempt to determine the nature of the degradation process.

B. DEGRADATION MEASUREMENTS

1. Procedures

The easiest method of obtaining a measure of the molecular weight of macromolecules in solution is by determining the intrinsic viscosity. Since the constants of the Mark-Houwink relationship for polyethylene-oxide in Water have been established (Eq. 3.8), changes in intrinsic viscosity can be used to quantitatively measure changes in the molecular weight of the polymer.

In this experiment, samples of the aqueous polyethylene-oxide solutions were withdrawn from the ¼-inch test pipe during flow tests. The extractor (Fig. 3) was driven by a 1 r.p.m. electric motor, so it obtained a 10 ml. sample in 30 seconds. This withdrawal rate was only 0.15 percent of the volume flow rate in the pipe at the lowest Reynolds numbers for which degradation measurements were made. No effects were noted in the pressure-transducer outputs during the extraction processes. Samples from the flow could be withdrawn from either the wall or the core region of the pipe, and from any of the pressure stations. The extractor had two interchangeable heads. In one, a size 18 hypodermic needle was cut to be flush with the wall of the pipe. In the other, the needle extended 0.06 in. into the .249 in. diameter pipe.

The intrinsic viscosities of samples withdrawn from the pipe were compared with those of the samples of the same test solutions which had been withdrawn from the reservoir. These

comparative measurements were made at about the same time, and normally within six hours of the flow tests. Thus, the only obvious difference in the samples was their flow history.

Solution viscosities were measured by use of two Cannon-Ubbelohde Dilution capillary viscometers (size 50) and a Cannon-Ubbelohde Four-Bulb Shear Dilution capillary viscometer (size 50) [10,14]. The measurements were made at 25.0 C in a Cannon Model M1 constant-temperature bath. The temperature control in this bath is rated $\pm$ 0.01 C. The flow times were measured by use of Standard Electric Timer Co. Type S-1 clocks which were readable to 0.01 sec.

(The importance of maintaining a constant temperature in order to obtain precise viscosity measurements can not be over-emphasized. Early in the course of this work, some undesirable variance was noted in the flow times of some calibration fluids, i.e. distilled water and sucrose solutions. It was finally determined that an almost imperceptible draft flowing over the inlet of the capillary viscometer caused the excessive experimental variance. The draft was produced by air emitted from the heating system for the building. When the exposed openings of the capillary tubes were covered with insulating cups, the excessive variance disappeared.)

Shin reported that he observed apparent degradation occuring in an Ubbelohde type viscometer for high molecular-weight solutions of polyethylene-oxide. When measurements on a sample were repeated, the flow times for successive runs were

consistently lower. He speculated that the degradation occurred as the solutions were rapidly drawn into the upper reservoir of the viscometer. Having been thus forewarned, special care was taken in the course of this work to fill the reservoir very slowly. Care was also exercised to avoid drawing air bubbles into the reservoir or the capillary tube. No evidence of degradation was observed when this procedure was followed.

The intrinsic viscosities were determined by using the methods proposed by Maron [42,43]. The single-point technique was used for the WSR-301 solutions with concentration of 50 wppm or less. Other methods for determing the intrinsic viscosity were also employed for several test solutions in order to compare the results [20,35,43,82]. It was found that in all cases the results of the various methods agreed to within two percent. The intrinsic viscosity measurements are considered accurate to four percent.

In order to determine if the extractor caused degradation, it was used to draw samples from a quiet reservoir. Comparative viscosity measurements were then made between the samples extracted thusly and the master solution. No significant difference was observed, indicating that the extraction process did not cause degradation, under these circumstances. While it is conceivable that the abrupt change in momentum the macromolecules experience in being withdrawn from pipe flow might cause degradation, the

decreased viscosity measured with flow length implies that degradation is occurring in the flow. The possibility that some fixed amount of degradation occurs in this extraction arrangement can not be excluded.

2. Results

The results of these degradation measurements are illustrated in Figs. 10, 11, and 12. The quantity $(1 - \frac{[\eta]}{[\eta]_o})100$ is used as a measure of the percent degradation. Here $[\eta]$ is the intrinsic viscosity of the sample extracted from the pipe, and $[\eta]_o$ is the intrinsic viscosity of the test solution withdrawn from the pressure reservoir.

In Fig. 10, the percent degradation for samples of 50 wppm WSR-301 solutions withdrawn from the wall region at Station 5 (753 diameters) is plotted versus the pipe Reynolds number.

In Fig. 11, the percent degradation is plotted versus the wall shear stress for the same samples. The plot appears to be roughly linear, but the experimental uncertainty is too great to establish any functional relationship.

Figure 12 shows the degree of degradation measured versus the distance of flow in the pipe at a pipe Reynolds number of 80,000. This plot also shows differences observed between samples withdrawn from the wall and from the core region of the pipe. These measurements indicate that the greatest rate of degradation occurs in the entry region of the pipe. In this region, the flow pattern

is greatly perturbed, so it is reasonable to assume that the macromolecules would be subjected to greater stresses, and thus experience greater degradation than further downstream. Further down the pipe,the higher viscosity measurements for the samples withdrawn from the core region may indicate that either there is less degradation in this region or that the macromolecules migrate away from the wall to a region of lower shear (or both). Possible supporting evidence for migration has been reported. Carver and Nadolink [11] observed that the polystyrene tracer particles which they used to facilitate photographing flow patterns tended to migrate to the pipe core in the flow of polyethylene-oxide solutions, whereas this phenomenon was not observed in water flow.

In the present work no change was observed in the character of the flow due to degradation as the fluid progressed downstream, i.e., the pressure measurements taken at the various stations during flow tests indicated that the gradient remained linear over the entire test length.

3. Relation Between Drag Reduction and Degradation

It may be seen in Fig. 4 that for Reynolds numbers greater than 30,000 the friction factors increased with increasing Reynolds number for the 1, 3, and 7.5 wppm solutions of WSR-301. It is tempting to attribute this upturn to a decreased molecular weight brought about by degradation. Unfortunately, experimental limitations associated with viscometry preclude accurate intrinsic viscosity measurements for such dilute solutions. For those

solutions with concentrations great enough to allow meaningful degradation measurements, (about 25 wppm and above), no upturn was observed. (These more concentrated solutions would probably also display increased friction factors at higher flow rates, where the degradation would presumably be more severe, or in longer pipes, wherein the fluid would be exposed to the turbulent shear field for a longer time.)

Figure 10 shows that, for a 50 wppm solution of WSR-301 in a ¼-inch pipe, degradation increases continuously with Reynolds number for Reynolds numbers greater than about 30,000. However, the fact that no lessening of the drag-reducting effectiveness for this 50 wppm solution was observed in this Reynolds number range cannot be taken as indicating that the degradation has negligible effect on the drag reduction. As discussed in a previous chapter, and as can be seen in Fig. 4, the drag-reducing effectiveness saturates for concentrations greater than about 10 wppm. At 50 wppm the presence of the polymer molecule in excess of the minimum amount required to produce maximum drag reduction would conceivably allow much degradation to take place without significant reduction in the drag-reducing properties of the solution.

On the other hand, there is evidence that the upturn observed of the less concentrated solution is related to the amount of degradation taking place. First, notice from Fig. 12 that the degree of degradation measured for the 25 and 50 wppm

solutions was very similar. It is, therefore, reasonable to assume that the less concentrated solutions degrade at similar rates. Assuming that solutions with concentrations less than the saturation value (about 10 wppm) follow a degradation pattern similar to that of the 25 and 50 wppm solutions, then the appreciable amount of degradation experienced at Reynolds numbers above 30,000 correlates directly with the increasing friction factors noted in Fig. 4 for these same Reynolds numbers.

As previously mentioned, some experimenters [17,33,45] have suggested, on the basis of indirect evidence, that drag reduction may be the direct consequence of molecular degradation. While the results of the present investigation do not rule out such a explanation, no evidence was found to indicate any such casual relationship.

Figure 13 shows the percent drag reduction versus Reynolds number for various concentrations of WSR-301. Comparing Figs. 10 and 13, it is seen that for 50 wppm of WSR-301 the amount of drag reduction experienced for Reynolds numbers above 30,000 is essentially constant while the amount of degradation increases continuously with increasing Reynolds number. Futhermore, it is seen from Fig. 13 that for the more dilute concentrations the percent drag reduction maximizes at a Reynolds number of 30,000. At this Reynolds number, the percent degradation is only 5 percent

and still rising. (Once more it has been assumed that these dilute solutions degrade in a manner similar to the 50 wppm solution.) Therefore, it appears improbable that the molecular degradation can be the sole cause of the drag reduction observed in polyethylene-oxide solutions.

Molecular degradation may, however, be a factor contributing to drag reduction. That is, the polymer molecule may absorb mechanical energy from small scale turbulent eddies or intense shear layers by breaking molecular bonds as well as through deformation. It is plausible that the probability of bond breaking increases as the molecules are increasingly deformed, which would presumably occur with increased turbulence at higher Reynolds numbers.

4. Measurements of Paterson and Fabula

As previously mentioned, the prior measurements of polymer degradation in flow were made by Paterson [55]. His experimental procedure was, in principle, the same as that employed in the present work, i.e., he measured changes in intrinsic viscosity and pipe friction factors for the flow of polyethylene-oxide solutions.

Paterson's viscosity measurements were made with a specially constructed low-shear, high-precision viscometer. As mentioned in Chapter 3, he observed a marked increase in the viscosity of WSR-301 at low shear rates. His observations in this regard are in accord with the prediction of Peterlin [56], but other investigators have not observed such effects for polyethylene-oxide solutions (Chapter 3).

The intrinsic viscosities reported for Paterson's WSR-301 solutions were roughly twice that reported by Fabula [17], Pruitt [60], or in this work.

The degradation measurements reported by Paterson agree qualitatively with those of this work, (i.e. the measured degradation increases with flow rate and flow distance, and the measured rates of degradation with flow distance are comparable.) However, where the results can be compared, his degradation measurements are about 50 percent higher than in the present work. This variance may be caused by the different pipe-entrance geometries. Paterson employed an abrupt, rough entrance whereas a conical adaptor was used in the present work.

Paterson withdrew samples from only the wall region of the flow, assuming that turbulent mixing would insure near homogeneity in the pipe. The present work showed a higher viscosity for solutions withdrawn from the core of the pipe than those withdrawn from the wall region.

For his pipe friction measurements, Paterson employed two differential transducers located 1327 diameters apart ($\frac{1}{4}$-inch diameter pipe) with the pressure taps at each station separated by 10 diameters. He claimed a 2 percent accuracy in his friction-factor measurements.

For those Reynolds numbers for which significant degradation was measured, Paterson consistently found a higher pressure gradient at his downstream station. The increase in pressure gradient (and thus friction factor) with flow distance would indicate that the character of the flow changes.

Fabula [17] noted a similar non-linear gradient for the flow of some of his polymer solutions, observing the non-linearity only in the first third of his pipe. His pressure versus flow-distance plots curved concave downward in this region, indicating increased friction in the flow direction. Fabula speculated that this might be caused by molecular scission, disentanglement, or both.

No evidence of such a change of pressure gradient was observed in the present work, even at the highest rates of flow. The different entrance geometries (Fabula also employed an abrupt contaction) may again account for this variance in the experimental observations.

C. THE NATURE OF THE DEGRADATION

It has been generally assumed that the degradation of long chain molecules in turbulent flow is caused mechanically, i.e., by the molecular stresses developed in hydrodynamic shear fields. However, it is not difficult to imagine other possible modes for degradation. For example, McGary [44] indicates polyethylene-oxide molecules in aqueous solutions degrade primarily by auto-xidation. Since entrapped air and metallic ions are normally present in abundance during pipe flow experiments, it is conceivable that turbulent mixing could significantly increase the reaction rate for the oxidation process. Also, there could be locally intense heating in the turbulent process, which may accelerate chemical degradation.

In order to obtain some measure of the relative magnitudes of the mechanical and oxidative degradation modes in pipe turbulence, the following experiment was conducted. Two identical solutions of 50 wppm WSR-301 were mixed. One mix was held under a vacuum of twenty-five inches of mercury for thirteen hours, then flow tests were conducted in the ¼-inch pipe with water-pumped nitrogen used to provide the driving pressure. The other solution was held in an atmosphere of compressed air under a pressure of twenty psig for fourteen hours, and then used in flow tests with compressed air providing the driving pressure. Samples of the solutions that had been subjected to turbulent flow were withdrawn from the pipe, and also samples of the solutions which were not subjected to turbulent flow were withdrawn from the tank. Viscosity measurements were then made with these samples, and no significant difference was noted between the "aerated" and the "deaerated" solutions. These results indicate that in the time scale of the flow tests, the oxidative degradation is not dominant, thus supporting the mechanical degradation concept.

A spectrographic experiment was then conducted to determine if the nature of any chemical reaction contributing to molecular scission might be revealed. A continuous-extraction column was used to remove the polyethylene-oxide from a solution of 100 wppm WSR-301 which had been degraded in turbulent pipe flow. The extraction process was conducted for some forty-eight hours. Then the benzene, which had been used as the stripping medium, was evaporated through the use of a vacuum rotary-evaporator, leaving small crystals of polyethylene-oxide resin.

An infra-red spectrum was obtained from this sample (in a potassium bromide pellet) and compared with that of a sample of the resin from which the original aqueous solution had been made. (The spectra were obtained using a Perkin-Elmer Model 337 Spectrophotometer.) Prominent bands in the reference sample were noted at the following wave numbers: 3450, 2950, 2850, 1450, 1430, 1340, 1320, 1270, 1230, 1140, 1090, 1050, 950, and 835 reciprocal centimeters. There was little difference in the spectrum obtained from the degraded sample above 1300 reciprocal centimeters, but new peaks were seen at 1000, 900, 860, 780, and 760 reciprocal centimeters. These bands correspond to absorptions of the extraction solvent. Of significance is the absence of absorptions at 1720-1680 reciprocal centimeters. This serves to confirm that the residue contained none of the reported [44] products from air oxidation. Of course, it is not known whether any gaseous products which may have evidenced this structure were lost.

Thus, the results of this experiment lend further support to the assumption that mechanical degradation is dominant for the turbulent flow of aqueous polyethylene-oxide solutions.

VI. VOLUME EQUIVALENCY NORMALIZATION

A. THE VOLUME EQUIVALENCY CONCEPT

Hoyt and Fabula [32,33] have demonstrated that significant drag reduction is observed in very dilute solutions of many different high polymer substances provided the molecular weight is above some minimum, (ca. 50,000). Furthermore, they established that, for a single class of polymer, the concentration required to achieve a given percent drag reduction decreases with increasing molecular weight.

These observations suggest that some parameter may be found which would allow normalization of the various concentration-molecular weight observations. Such a parameter might also provide some insight leading to a better understanding of the drag-reduction phenomenon itself.

During the course of this work, it was found that the relative volume of solution "occupied" by the polymer molecules is apparently an important parameter relating to the drag-reduction phenomenon. The basis for the determination of this volume occupied is Tanford's "equivalent hydrodynamic sphere" (Chapter 3).

The equivalent hydrodynamic sphere is used to represent the volume dominated by the polymer macromolecule and the associated entrapped solvent. The volume occupied by equivalent spheres per unit volume of solution will be called R_v, the "effective volume ratio". Polymer solutions containing different molecular weight species of the same polymer type are called "volume equivalent" if they have the same R_v.

The effective diameter of the equivalent sphere is, from Eq. (3-7),

$$D_{eff} = \gamma \langle r^2 \rangle^{\frac{1}{2}} . \tag{6-1}$$

The effective volume per molecule, V_{eff}, is then

$$V_{eff} = \frac{\pi}{6} D_{eff}^3 = \frac{\pi}{6} \gamma^3 \langle r^2 \rangle^{3/2} . \tag{6-2}$$

From Eq. (3-6),

$$\langle r^2 \rangle^{3/2} = \frac{[\eta]_M}{\Phi} , \tag{6-3}$$

so,

$$V_{eff} = \frac{\pi}{6} \gamma^3 \frac{[\eta]_M}{\Phi} , \tag{6-4}$$

since the number of molecules per unit volume is c A/M, where A is Avogadros' number, the effective volume ratio, R_v, is,

$$R_v = V_{eff} \frac{c A}{M} = \frac{\pi}{6} \frac{A}{\Phi} c \gamma^3 [\eta]. \tag{6-5}$$

Since Φ is a constant, polymer solutions are volume equivalent when the product $\gamma^3 c[\eta]$ is constant. (The values of γ for polyethylene-oxide in water are obtained from Eq. (3-10).) From Eqs. (3-11) and (6-5) it can be seen that dilute polymer solutions are also volume equivalent when the concentrations are the same percentage of the critical concentration for the polymers. (For polyethylene-oxide, the critical concentrations may be estimated from Eq. (3-12).)

It is hypothesized that the effective volume ratio is a dominant parameter governing the flow properties of dilute polymer solutions. It follows that volume equivalent solutions should display the same flow properties. Furthermore, the effective volume ratio should serve as a normalizing parameter for various concentration-molecular weight combinations for a given class of polymer.

B. TESTS OF THE VOLUME EQUIVALENCY HYPOTHESIS

Some data can be found in the literature which can be used to test the hypothesis that the effective volume ratio serves as a normalizing parameter for solutions of polyethylene-oxide in water.

Figure 14 shows drag reduction measured by Hoyt [32] in his turbulent-flow rheometer as a function of molecular weight for various concentrations of polyethylene-oxide polymers. Hoyt used these results to demonstrate that if his rheometer is calibrated with known molecular weight samples of a polymer class then it could be used to estimate the molecular weight for other polymers from drag measurements alone.

Figure 15 illustrates how the volume equivalency concept can serve as a normalizing parameter for Hoyt's data. The points plotted in Fig. 15 were obtained in the following manner: For a given percent friction reduction in Fig. 14, (taken at intervals of 10-percent friction reduction), a horizontal line was drawn to intersect the curves corresponding to various polymer concentrations.

At these various intersections, the corresponding polymer molecular weight can be read on the absissa. Equation (3-8) was then used to find the associated intrinsic viscosities. With the values of intrinsic viscosity, the critical concentration is obtained by the use of Eq. (3-12). The scatter in the resulting plot (Fig. 15) is about the same as that in Hoyt's original work and it is seen that all the data does indeed fall on a single curve.

Fabula [17] and Paterson [55] reported their intrinsic viscosity measurements for the various polyethylene-oxide blends which they tested in pipe flow experiments. This allows a further test of the volume equivalency concept. The following tabulation gives the measured intrinsic viscosities, the corresponding γ^3 (from Eq. (3-10)),and C_c' (from Eq. (3-12)) for the various experiments.

Investigator	Polymer	$[\eta]$	γ^3	C_c', wppm
Paterson	WSR-301	28.0	0.835	204
	WSR-205	5.5	0.766	1160
	WSR-35	3.0	0.741	2220
Fabula	WSR-301	16.0	0.812	371
	WSR-205	3.2	0.743	2075
	WSR-35	1.7	0.698	4080
Present Work	WSR-301	13.5	0.806	440
	WSR-205	2.5	0.730	2700
	WSR-35	1.1	0.683	6500
	WSR N-3000	2.8	0.736	2400

For Paterson's work, the solution concentration ratios required for volume equivalence for his 301/205/35 blends are 1.0/5.5/10.9. For Fabula's samples, the corresponding ratios are also 1.0/5.5/10.9. The concentration ratios to produce volume equivalent solutions from the blends used in the present work were 1.0/6.2/14.9. (The WSR-205 and WSR-35 blends used in this work are at least five years old, and the low intrinsic viscosity readings probably indicate degradation. Pruitt [60] has previously reported degradation of polyethylene-oxide resins with age.)

Figure 16, based upon representative data from Fabula for solutions which are approximately volume equivalent, shows that such solutions displayed nearly the same frictional resistance. Figures 17 and 18, taken from Paterson for solutions which, fortuitously, also nearly fulfill the equivalent volume criterion, show further evidence of the volume equivalency effect. Figures 19 and 20 show similar results obtained in the present work.

C. DISCUSSION OF RESULTS

Figures 14 - 20 provide substantial evidence in support of the contention that the volume equivalency concept provides a means to unify many observations from flow experiments of various concentration-molecular weight combinations for commercial blends of the WSR- series of polyethylene-oxide.

Figure 15 demonstrates that the many curves of Hoyt's plot (Fig. 14) can be collapsed onto one curve if the effective volume ratio is used. Hoyt's data were obtained from measurements at a Reynolds number of 14,000 in a 0.048-inch diameter tube.

Figure 16 is based on data from Fabula [17] for polymer concentrations which nearly fulfill the equivalent volume criterion. His flow tests were conducted in a 1.02-cm. pipe, and the intrinsic viscosities of the polymer blends used were measured by representatives of the manufacturer .

The data plotted in Figs. 17 and 18 are representative points taken from continuous curves in Paterson's report [55], again for relative concentrations nearly fulfilling the equivalent volume criterion. This plot is based upon flow experiments in a 3/4-inch diameter pipe. Further supporting evidence (not shown in this paper) for the volume-equivalency concept may be seen for some of his results obtained in a ¼-inch pipe. Of particular note in Figs. 17 and 18 is the fact that the "onset" of drag reduction, i.e. the points where the polymer data departs from the Prandtl curve, occurs at about the same Reynolds numbers for solutions that are nearly volume equivalent.

Figures 19 and 20 are based upon results of the present work. It may be seen that the similar pipe-friction measurements obtained for volume-equivalent solutions extends over a wide range of Reynolds numbers. Of particular note is the similarity in the transition region of these plots. This similarity was also noted in the output from the pressure transducers during flow tests made in the transition region.

The nature of the mixes compared in Fig. 19 further emphasizes the importance of the volume effects. In the associated experiment, mixes composed of a combination of 3 wppm WSR-301 and 25 wppm WSR N-3000 were compared with volume equivalent solutions of 7.5 wppm WSR-301. The similar frictional resistance over nearly two decades of Reynolds numbers in this case where the solutions contained polymers with presumably different molecular weight distributions further demonstrates the importance of the volume effects.

Thus, from data selected to show the effects of volume equivalence, there is considerable evidence indicating that the effective volume ratio is an important parameter governing the pipe-friction for the flow of WSR-series solutions of polyethylene-oxide. These data are based upon the independent work of four investigators, and cover a wide range of Reynolds numbers and pipe diameters. The maximum variance in the percent drag-reduction observed for volume equivalent solutions was about 8 percent.

The lessening of drag-reducing effectiveness with degradation can be qualitatively explained as a decrease in the effective volume ratio for the degraded solution. When the polymer solution degrades, the intrinsic viscosity and γ^3 (Eq. (3-10)) are both reduced, while the concentration remains unchanged. Thus, from Eq. (6-5), the effective volume ratio of the polymer solutions is reduced.

Two degraded solutions were tested during the course of this work. The associated measurements can be used to quantitatively test the volume-equivalency hypothesis for degraded solutions.

The intrinsic viscosity changed from 13.4 to 9.3 for a 50 wppm mix after it had flowed through the ¼-inch pipe and had been caught in containers. The critical concentration associated with an intrinsic viscosity of 9.3 is 660, whereas that for $[\eta]$ = 13.4 is 446. Thus, the 50 wppm degraded solution would be volume equivalent to a 33.8 wppm solution of nondegraded WSR-301. Such concentrations are in the saturation range for drag reduction (Fig. 13), so the maximum drag reduction attained should yet be observed. However, in the Reynolds number range of the test (30,000-90,000 in the ¼-inch pipe), the degraded solution displayed a 68 percent drag reduction whereas that for the non-degraded solutions was 74 percent. Similarly, a 25 wppm solution that was degraded to an $[\eta]$ of 9.4 should be volume equivalent to a 17.5 wppm nondegraded solution. This latter concentration is also in the saturation range, but the degraded solution displayed a lessening of drag reduction from 74 to 65 percent in the same 30,000-90,000 Reynolds number range. Thus, while the volume equivalency concept can provide a good estimate of the pipe friction even for degraded solutions, the agreement is not as good as for non-degraded solutions.

It was also found that the WSR N-series polymers are not in general as effective as the WSR- series for apparently equivalent volumes. This may be due to different molecular-weight distributions in the two series. As previously mentioned, the WSR- series is thought to have a high molecular weight tail, whereas the WSR N-series has a narrower distribution with the high molecular-weight tail missing.

A degraded solution would almost certainly have a different molecular-weight distribution than its nondegraded counterpart. Further, the most significant change may occur with the highest weight components.

Thus, while the results of this work indicate that the effective volume ratio is the dominant parameter, the tests with degraded WSR-301 and the nondegraded WSR N solutions indicate that the molecular-weight distribution may also be important, but this importance appears to be secondary. (Based on measurements of degraded solutions, Paterson concluded that drag-reduction does not correlate directly with the intrinsic viscosity of the solutions, and speculated that the molecular-weight distribution was an important factor.) It is possible that the calculated relative volume (based on viscosity measurements and the equivalent hydrodynamic sphere representation) does not reflect the effective volume the molecules occupy in the same manner for polymers having different molecular-weight distributions.

The great difference in the intrinsic viscosity measurements by Paterson and those reported by Fabula and in the present work are disturbing. The close similarity in the concentration ratios for the various polymer types to obtain volume equivalence, and the close agreement in the frictional resistance measurements indicates that the differences must lie primarily in the viscometery and not in the polymer blends.

The effective-volume ratio hypothesis, while not providing a mechanism whereby the macromolecules alter the flow properties of the solutions, does show that the details of the structure of the macromolecule and its size may not be of primary importance in determining the amount of drag reduction which will occur.

The fact that solutions of polyethylene-oxide which have equivalent macromolecular volumes display similar pipe-friction reducing properties is somewhat analogous to Einstein's findings [16]. Einstein showed that for rigid spheres in dilute solution (no interactions between particles), the specific viscosity of the solution is determined by the volume fraction occupied by the spheres, and is independent of the size of the individual spheres. (Viscosity predictions based on Einstein's equation are good up to a volume fraction on the order of ½-1 percent.) Generalizing for polymer solutions, perhaps the hydrodynamically equivalent volumes similarly determine flow properties.

This work has demonstrated that solutions which have the same volume ratio of polyethylene-oxide molecules possess similar gross flow characteristics. It is not known whether other flow characteristics (e.g., turbulent structure, velocity profiles, etc.) are also similar.

The volume effects have heretofore been largely ignored. The observations of this experiment may provide a significant clue to aid in finding a mechanism to explain the drag-reduction phenomenon. If similar volume correlations could be found for other polymers,

perhaps comparisons among the various drag-reducing additives may reveal further parameters (e.g., chain flexibility, molecular weight distribution, etc.) that are important in the flow properties of these solutions. Perhaps an understanding of the relative importance of the various associated parameters will lead to an understanding of the drag-reduction phenomenon itself.

VII. SUMMARY AND CONCLUSIONS

During the course of this experimental study of the pipe-frictional properties of aqueous polyethylene-oxide solutions, many aspects of the drag-reduction phenomenon were investigated. Pipe-friction factors were determined over a range covering two decades in Reynolds numbers, including the transition and well into the fully turbulent regimes. Three test pipes having different diameters were employed. Pressure measurements were obtained at a number of points along the length of the pipes in order to determine the nature of the pressure gradient under a variety of flow conditions. Strain-gage pressure transducers with interchangable pressure diaphragms were employed to obtain high accuracy in the measurements over a wide range of pressures.

Special emphasis was placed on uniform and gentle handling procedures for the polymer solutions. Standard mixing, flow-test, and viscosity measurement techniques were used. The fluids actually tested in the pipe flow experiments were characterized by intrinsic viscosity determinations.

Intrinsic viscosity measurements were also made for samples withdrawn from pipe flow at several points under various flow conditions to obtain a determination of polymer degradation during pipe flow. The nature of the polymer degradation was also studied by use of spectrographic techniques.

The following is a summary of observations and conclusions based upon the results of this experiment.

1. The measured changes in intrinsic viscosity of solutions subjected to flow provide direct evidence that polyethylene-oxide molecules do degrade in turbulent pipe flow. There is no evidence of chemical reactions causing the degradation and thus it can be concluded that the degradation is caused primarily by mechanical means.

2. The measured degradation increased with flow rates. The greater degradation correlates with a lessening of drag-reduction effectiveness observed in flow test of the more dilute polymer solutions.

3. The higher viscosity observed for polyethylene-oxide solution samples withdrawn from the core compared with those taken from the wall region indicate either greater degradation in the wall region or particle migration to the core of the pipe, or both. Photographic evidence from an independent source supports the migration hypothesis.

4. Pipe-entrance losses for polyethylene-oxide solutions are greater than for water. The higher entrance losses occur even though the pipe-friction for the same solutions is reduced by 75 percent.

5. The observed effect upon the transition from laminar to turbulent flow due to the presence of polyethylene-oxide additive is summarized as follows:

a. The Reynolds number corresponding to the onset of intermittency decreases with increasing polymer concentrations.

b. The Reynolds number range over which intermittency occurs decreases with increasing polymer concentration.

c. The magnitude of the pressure fluctuations are independent of polymer concentration.

d. If the onset critical wall shear stress is exceeded at Reynolds number below that wherein transition would normally occur, no marked transition occurs.

6. The "diameter effect" observed in the flow of polyethylene-oxide solutions can be attributed to differences in wall shear stresses. At Reynolds numbers where the wall shear stress is large compared with the critical value, the pipe-friction is the same for pipes of various diameters.

7. The results of this work further support Virk's observation that the wall shear stress is a dominant parameter governing the onset of drag reduction. The observations in this study also support Paterson's findings that the critical wall shear stress is not independent of concentration. In general, the critical wall shear stress decreases (slightly) with increasing polymer concentration.

8. It has been found in this work that the effective volume ratio is a dominant parameter affecting pipe-frictional resistance for aqueous polyethylene-oxide solutions. Further, it has been found that volume equivalence, based upon the effective volume ratio, can serve as a unifying parameter for pipe-friction measurements over a wide range of flow conditions.

9. Some evidence was found that the molecular weight distribution of the polymers in solution is also an important parameter, but it is of secondary importance compared with the volume effects.

10. The volume equivalence hypothesis, while not providing a mechanism whereby the macromolecules alter the flow properties of the solution, does show that the details of the structure of the macromolecule and its individual size may not be of primary importance in determining the amount of drag reduction which will occur. It may be that molecules without linear structure would produce drag reduction if they were to occupy the same relative volume as the linear molecule.

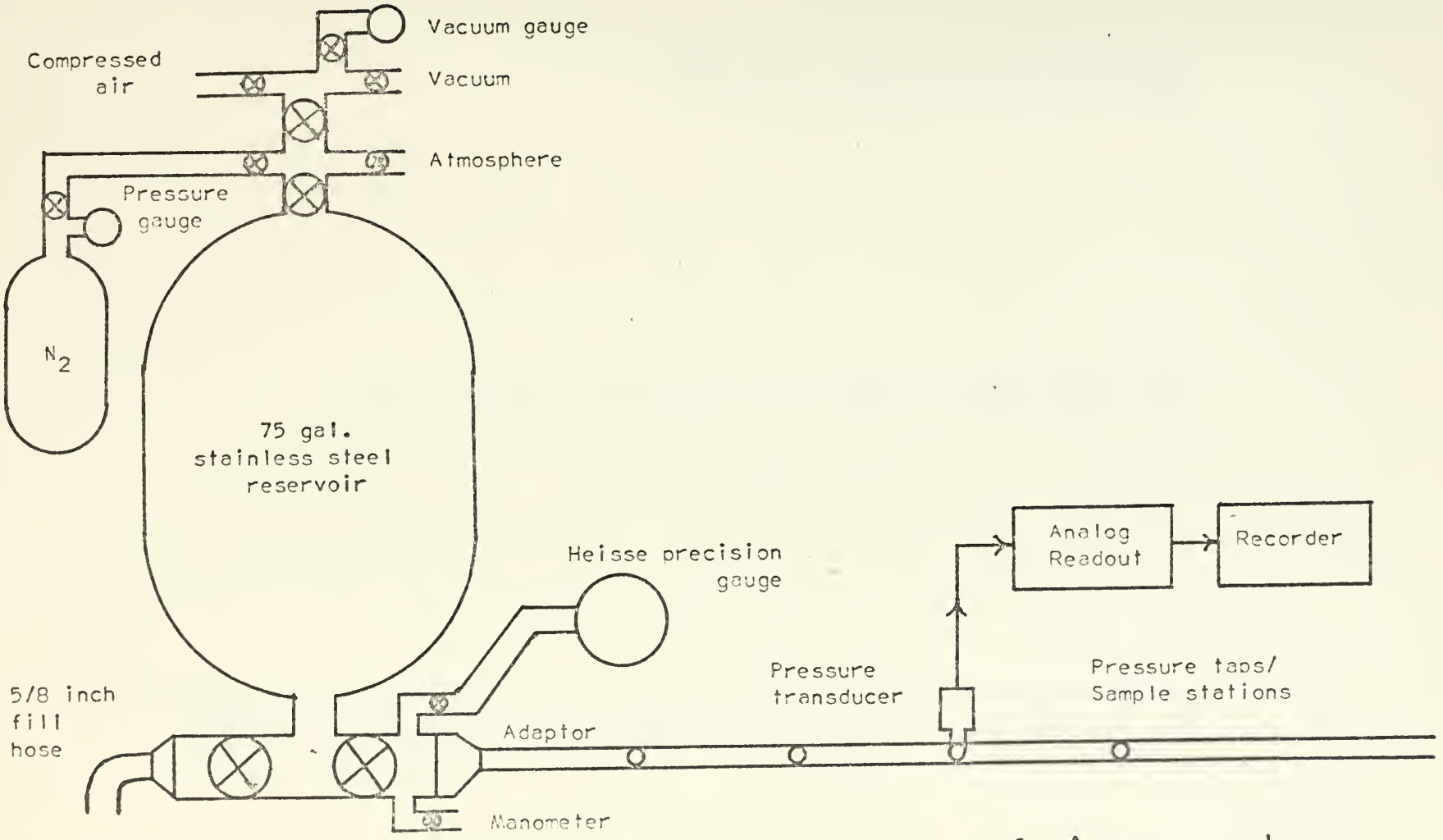
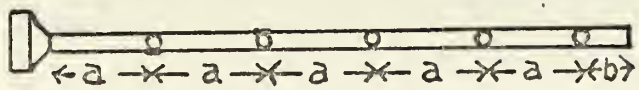


Figure 1: Schematic Diagram of Apparatus for Pipe-Flow Tests



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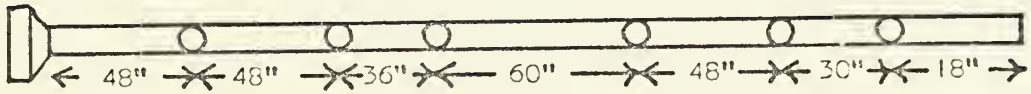
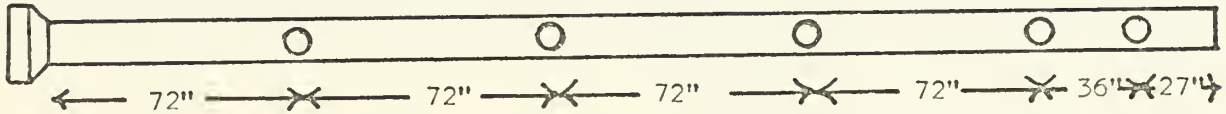
(a= 37.5 in.
b= 16.5 in.)



0.394 in. dia. x 24.0 ft.



0.775 in. dia. x 29.25 ft.

Figure 2: Test pipes

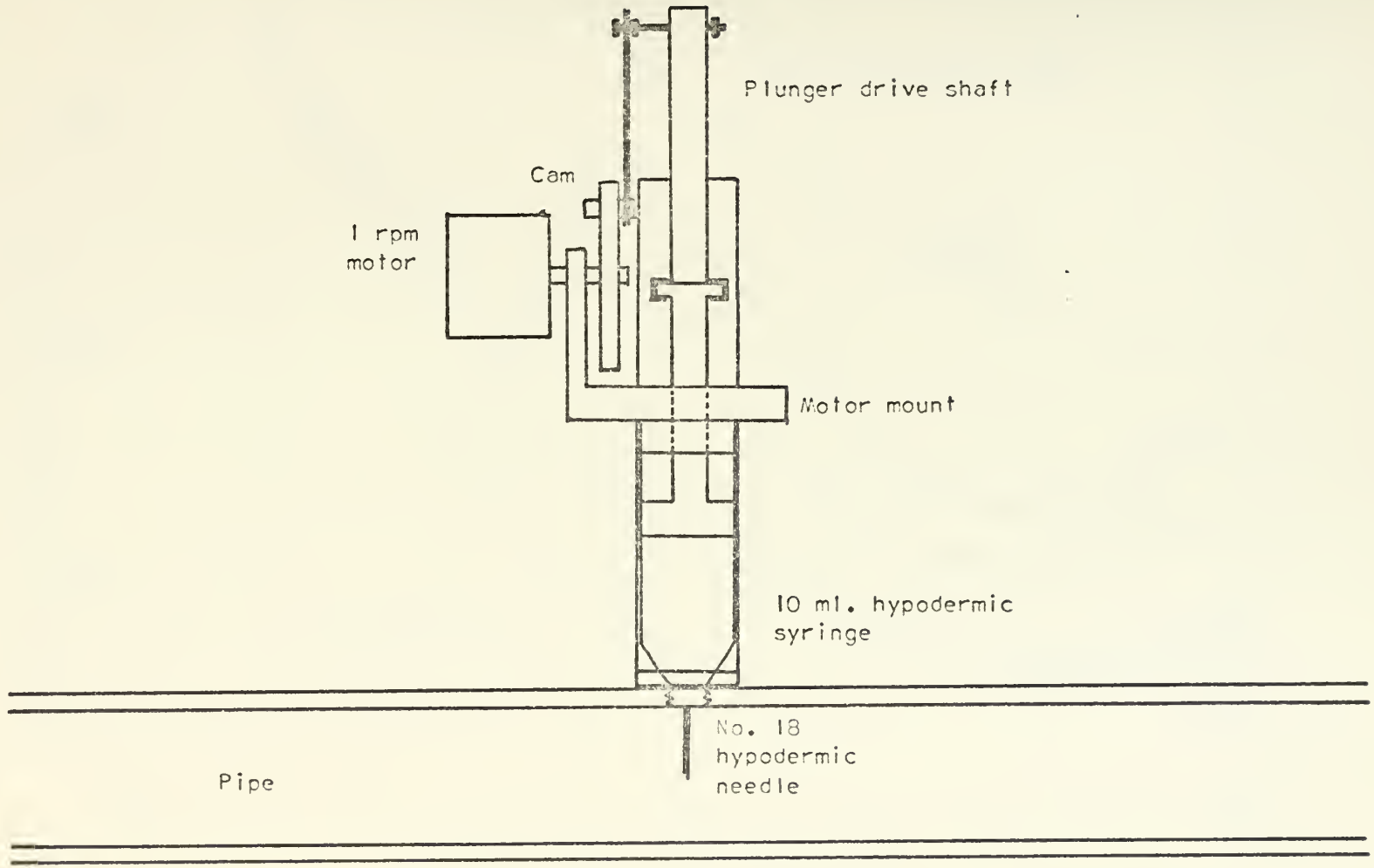


Figure 3: Sample Extractor

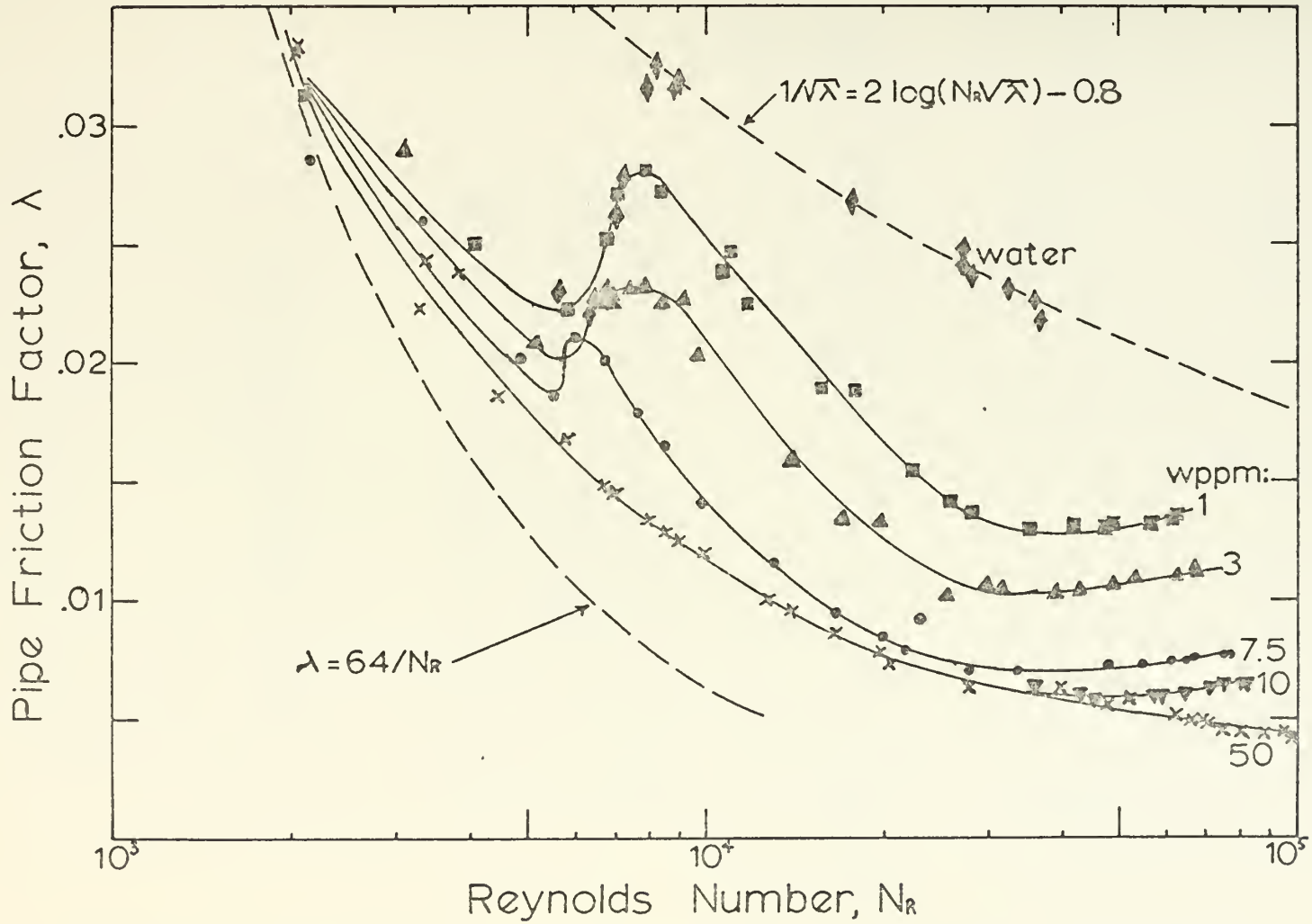


Figure 4: Frictional Resistance for various concentrations of WSR-301 (.249 in. pipe)

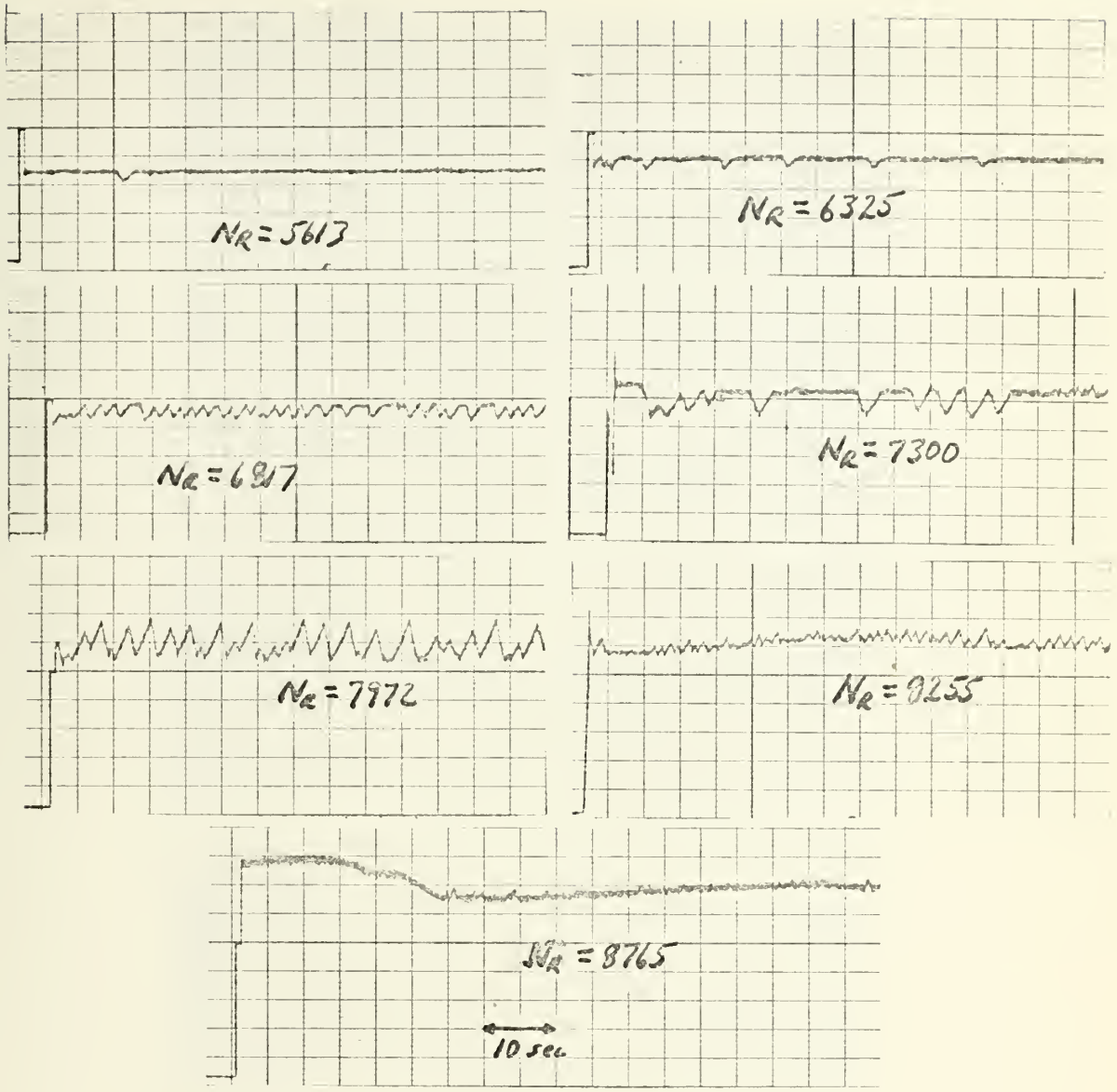


Figure 5: Representative transducer outputs displaying intermittency in the flow of water.

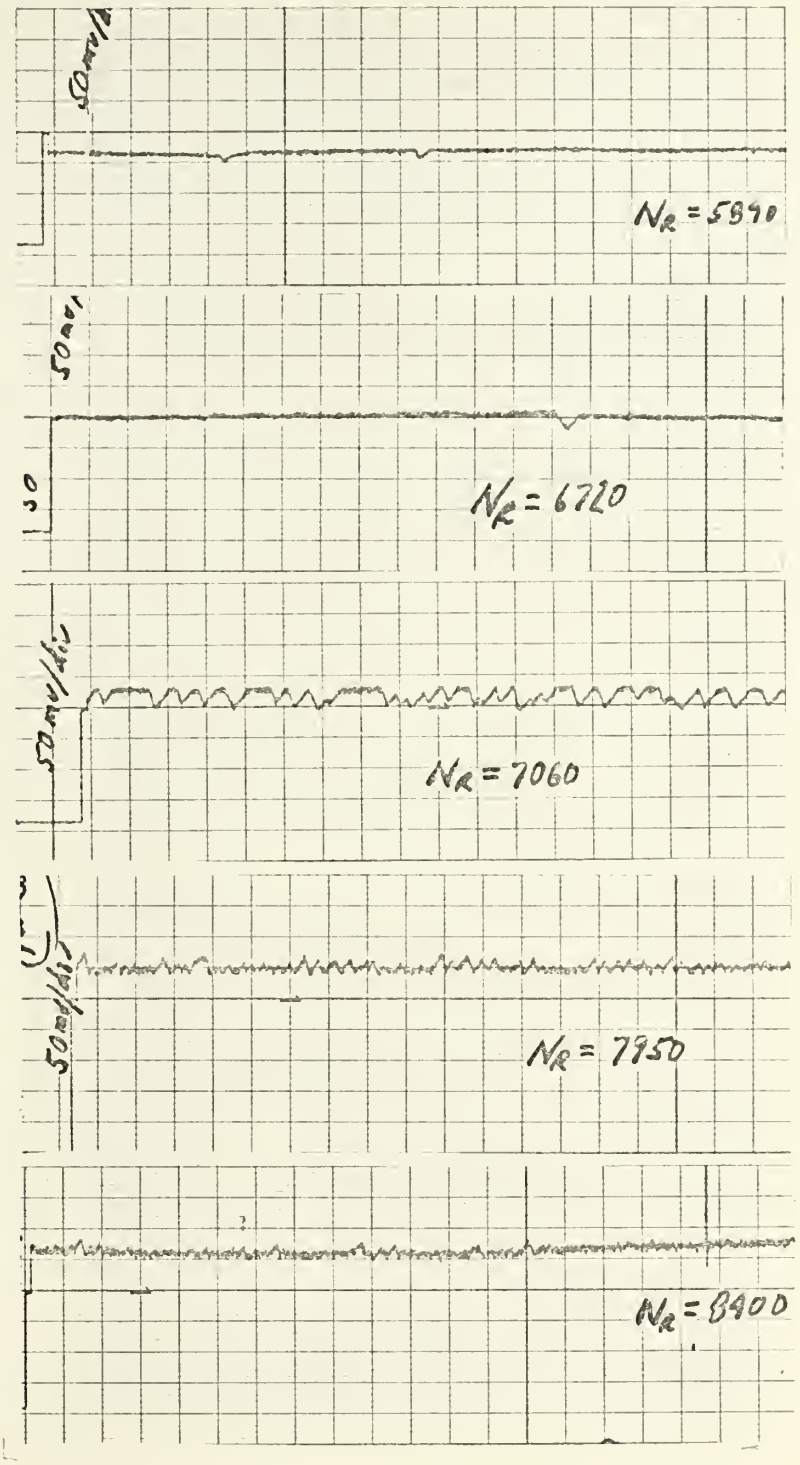


Figure 6: Representative transducer outputs displaying intermittency in the flow of a 1 wppm WSR-301 solution.

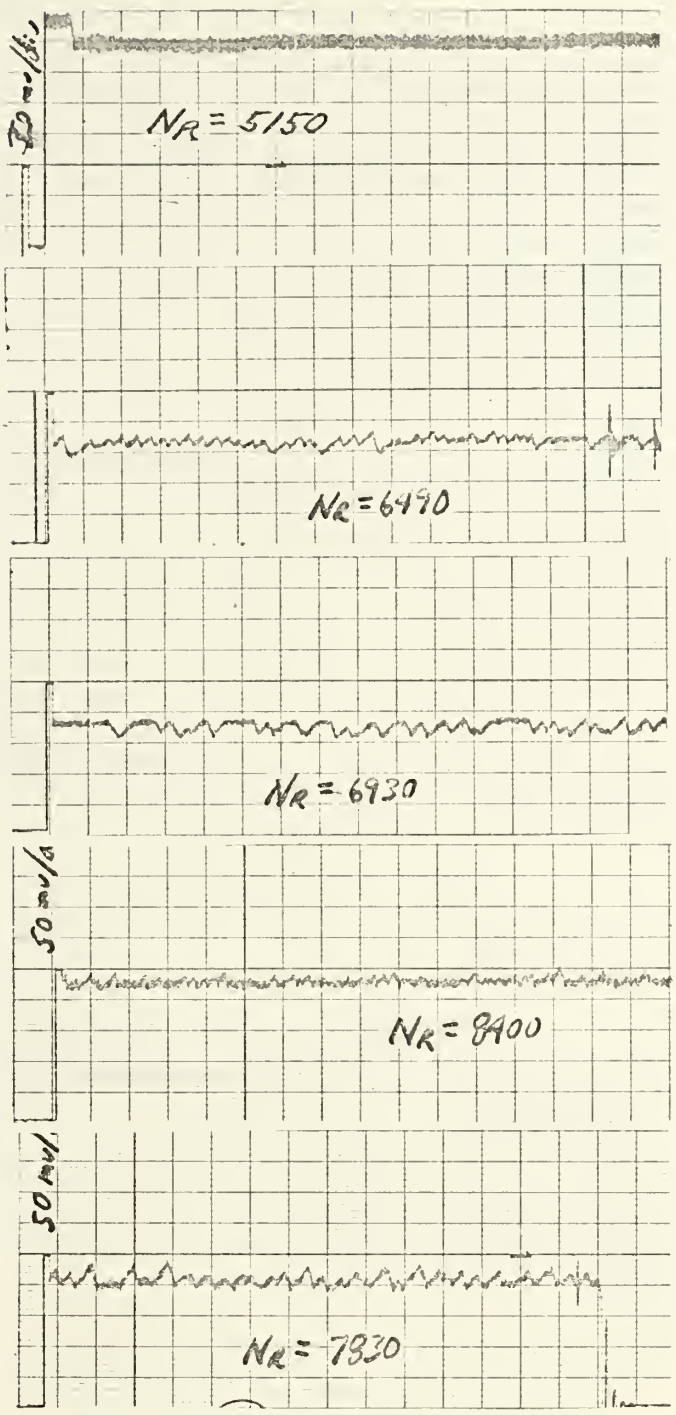


Figure 7: Representative transducer outputs displaying intermittency in the flow of a 3 wppm WSR-301 solution.

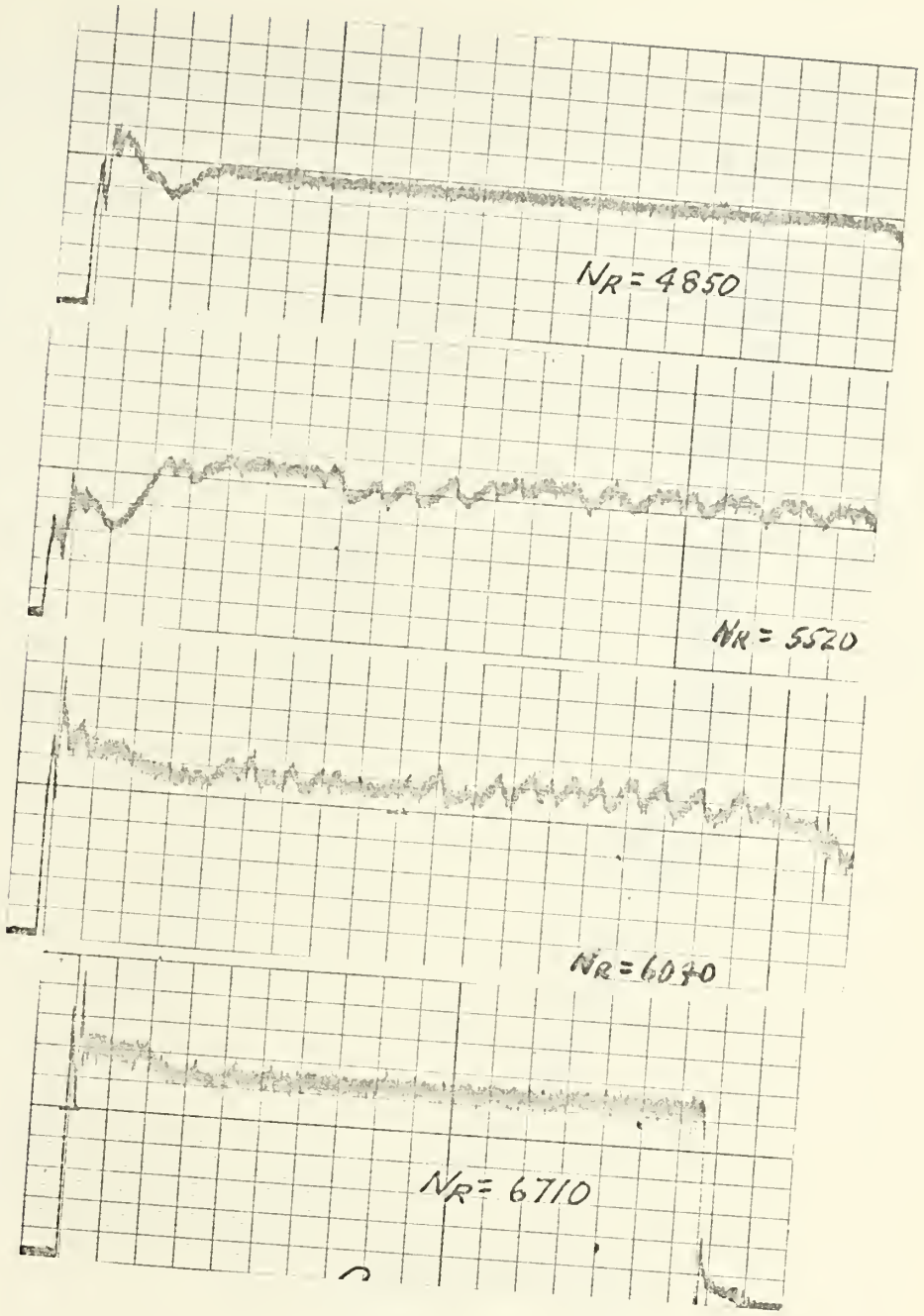


Figure 8: Representative transducer outputs displaying intermittency in the flow of a 7.5 wppm WSR-301 solution.

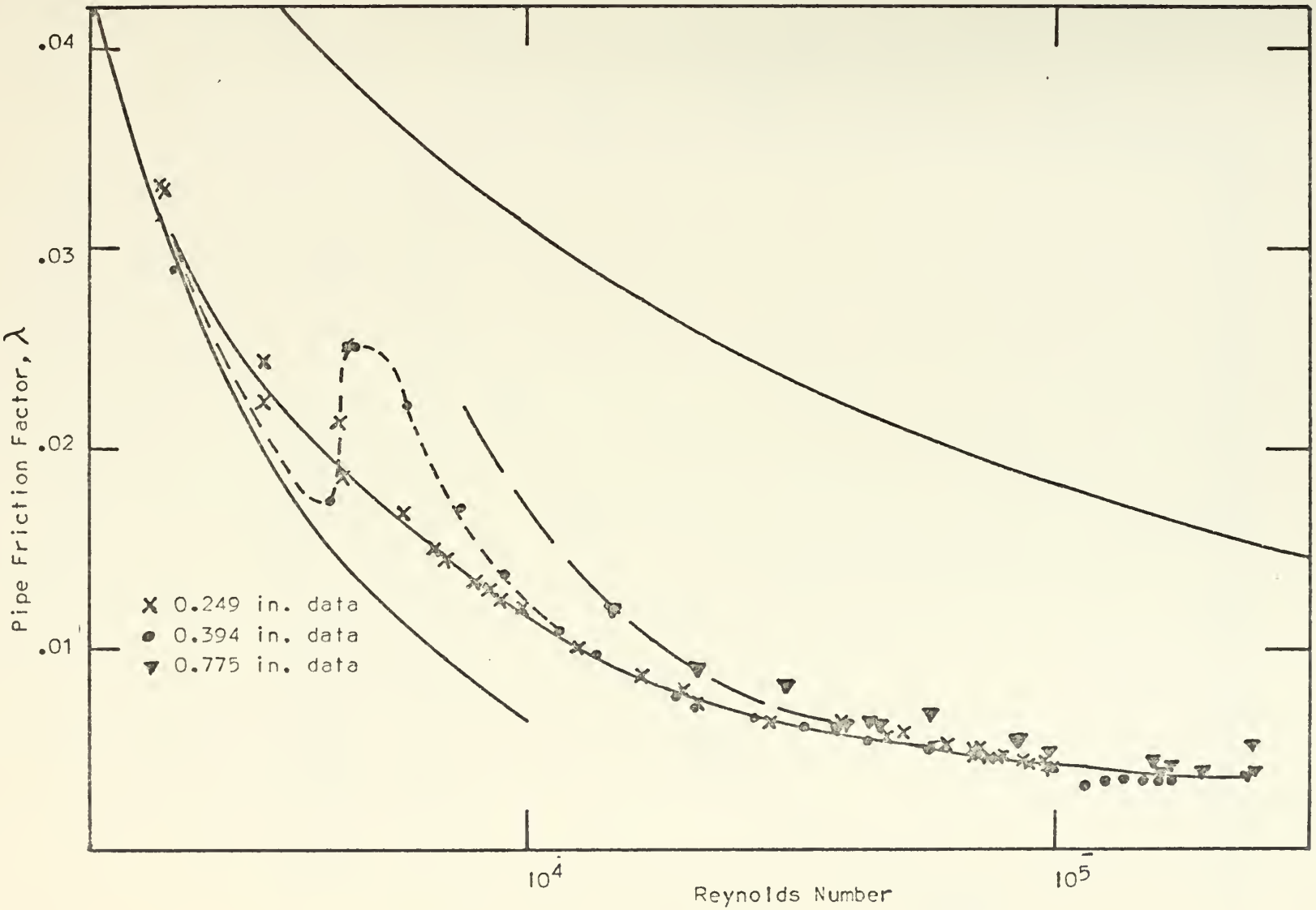


Figure 9: Frictional resistance for 50 wppm WSR-301 in pipes with various diameters

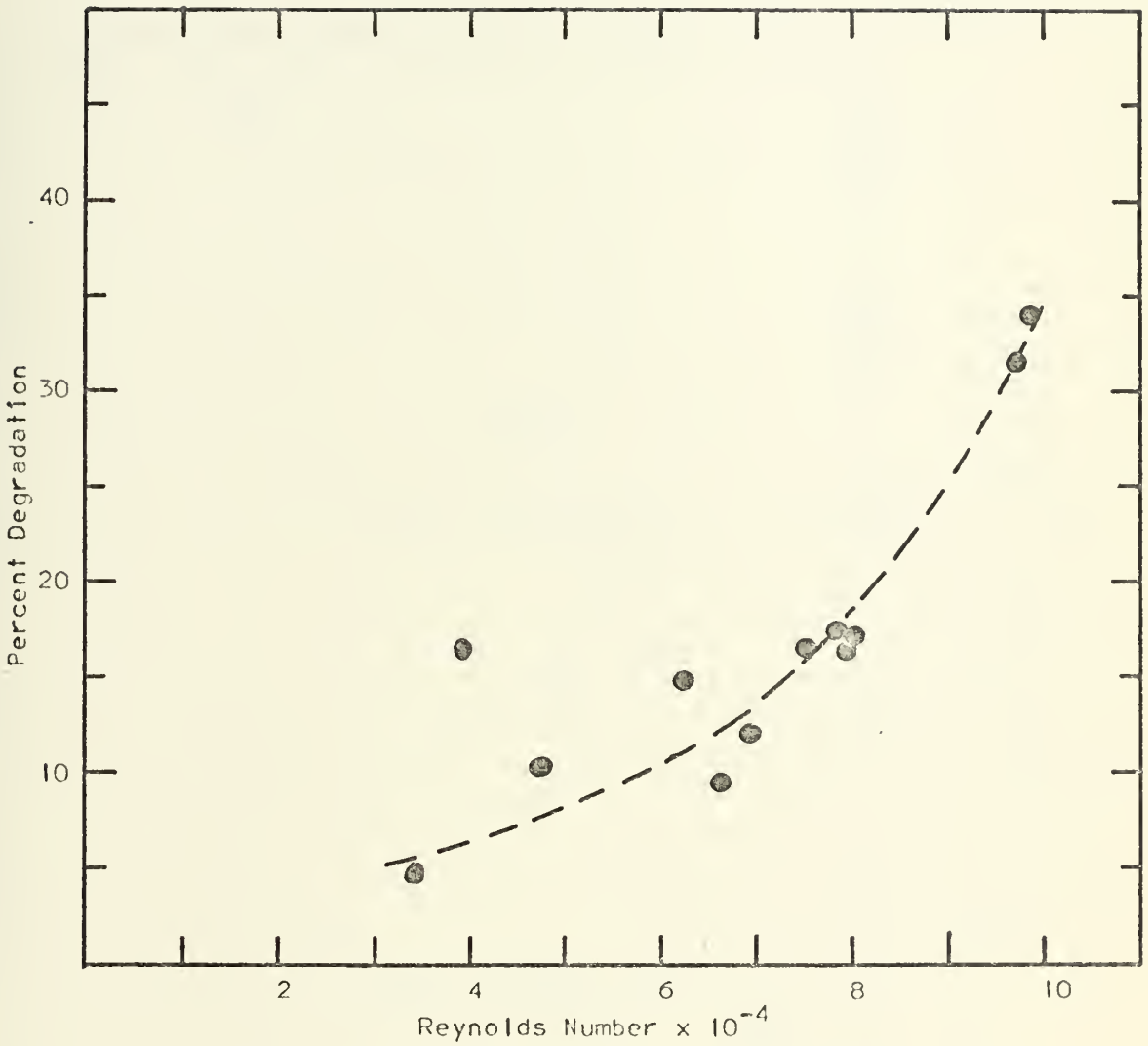


Figure 10: Degradation vs. Reynolds number for 50 wppm WSR-301. Samples withdrawn from $\frac{1}{4}$-inch pipe wall region, 753 diameters from entrance.

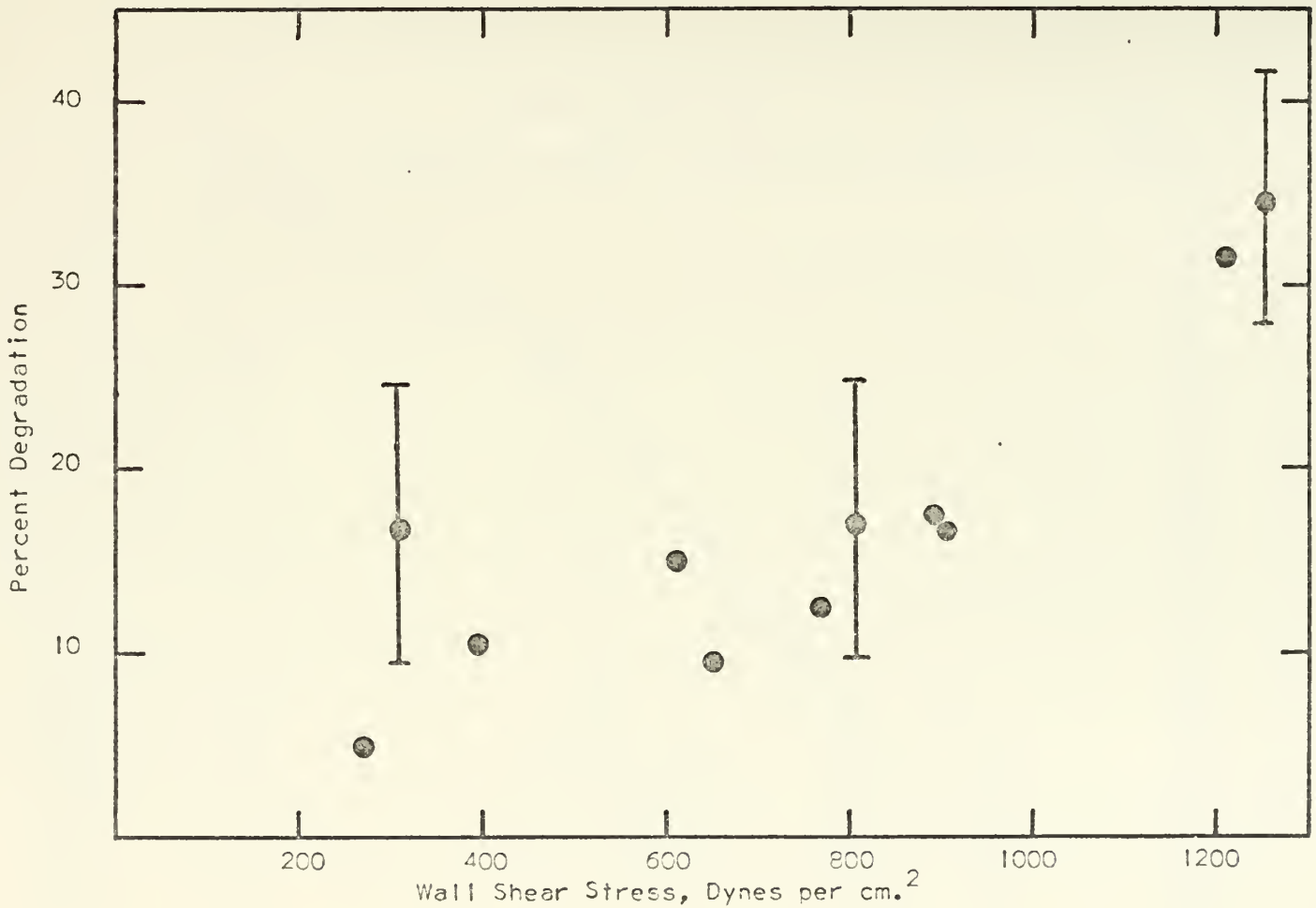


Figure 11: Percent polymer degradation vs. wall shear stress for 50 wppm WSR-301. Samples were withdrawn from wall region of $\frac{1}{4}$-inch pipe at 753 diameters from entrance.

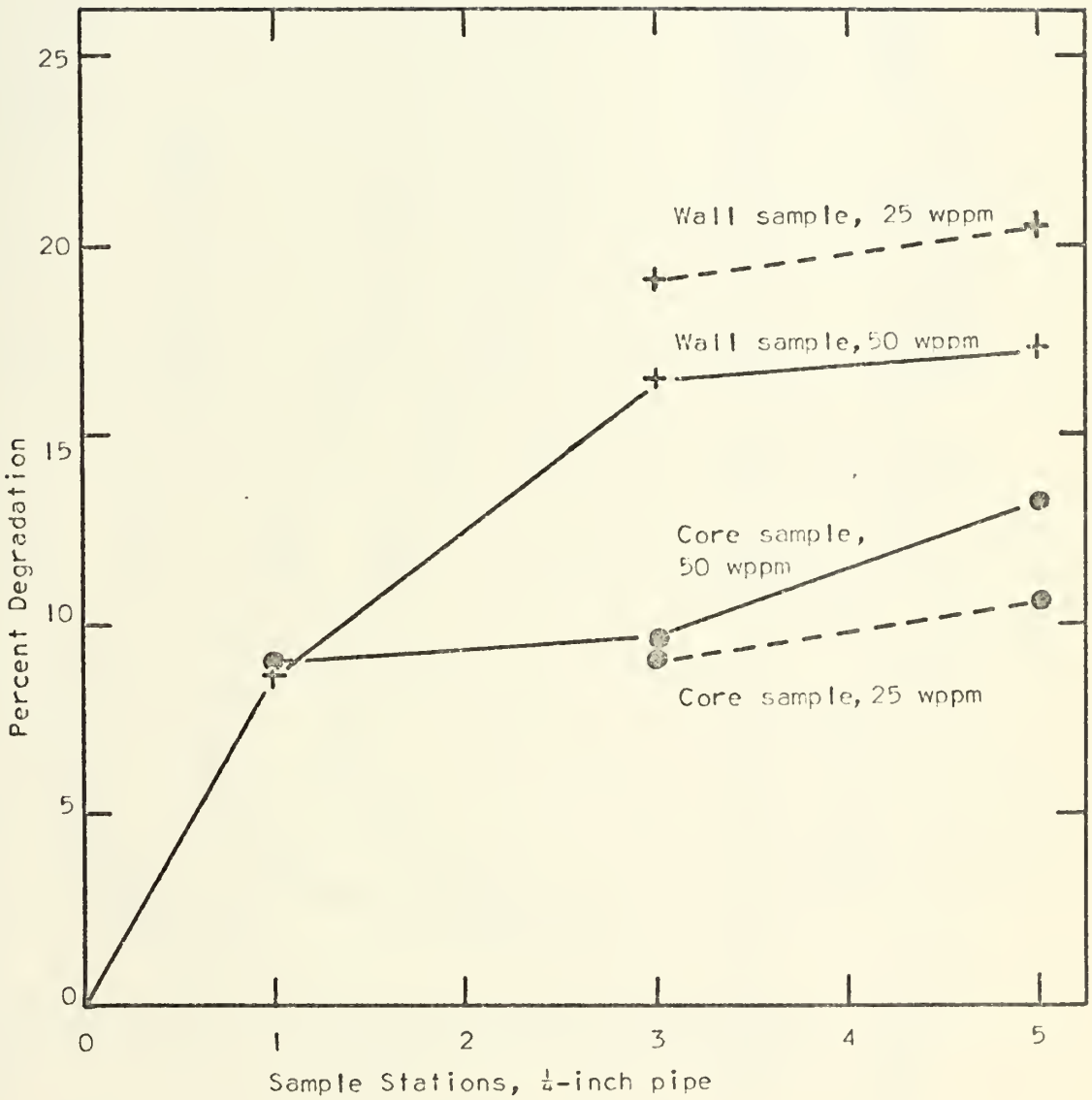


Figure 12: Percent polymer degradation vs. flow distance in ¼-inch pipe for 25 and 50 wppm WSR-301 solutions. Reynolds number= 80,000.

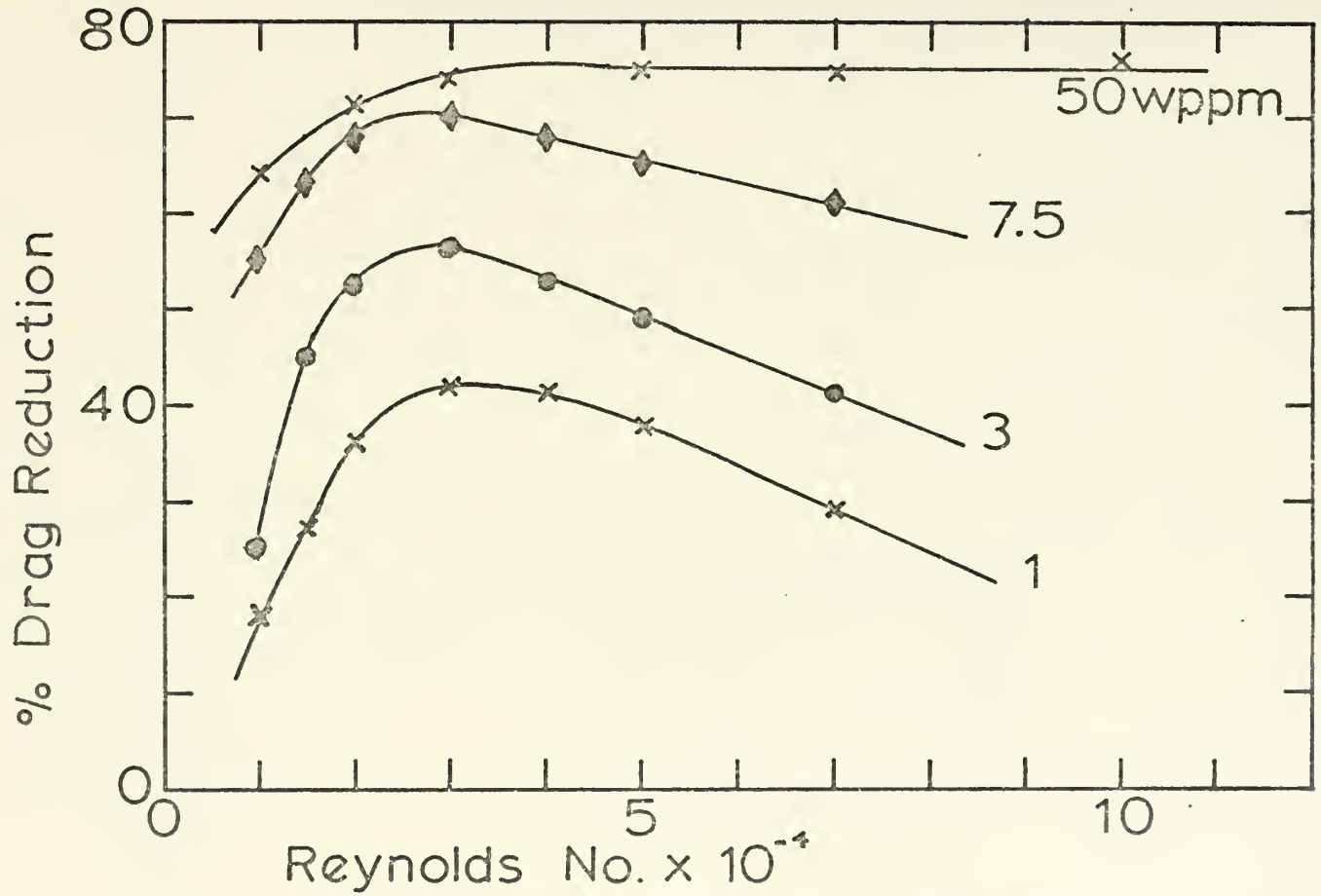


Figure 13: Drag reduction for various concentrations of WSR-301 (1/4 in. pipe)

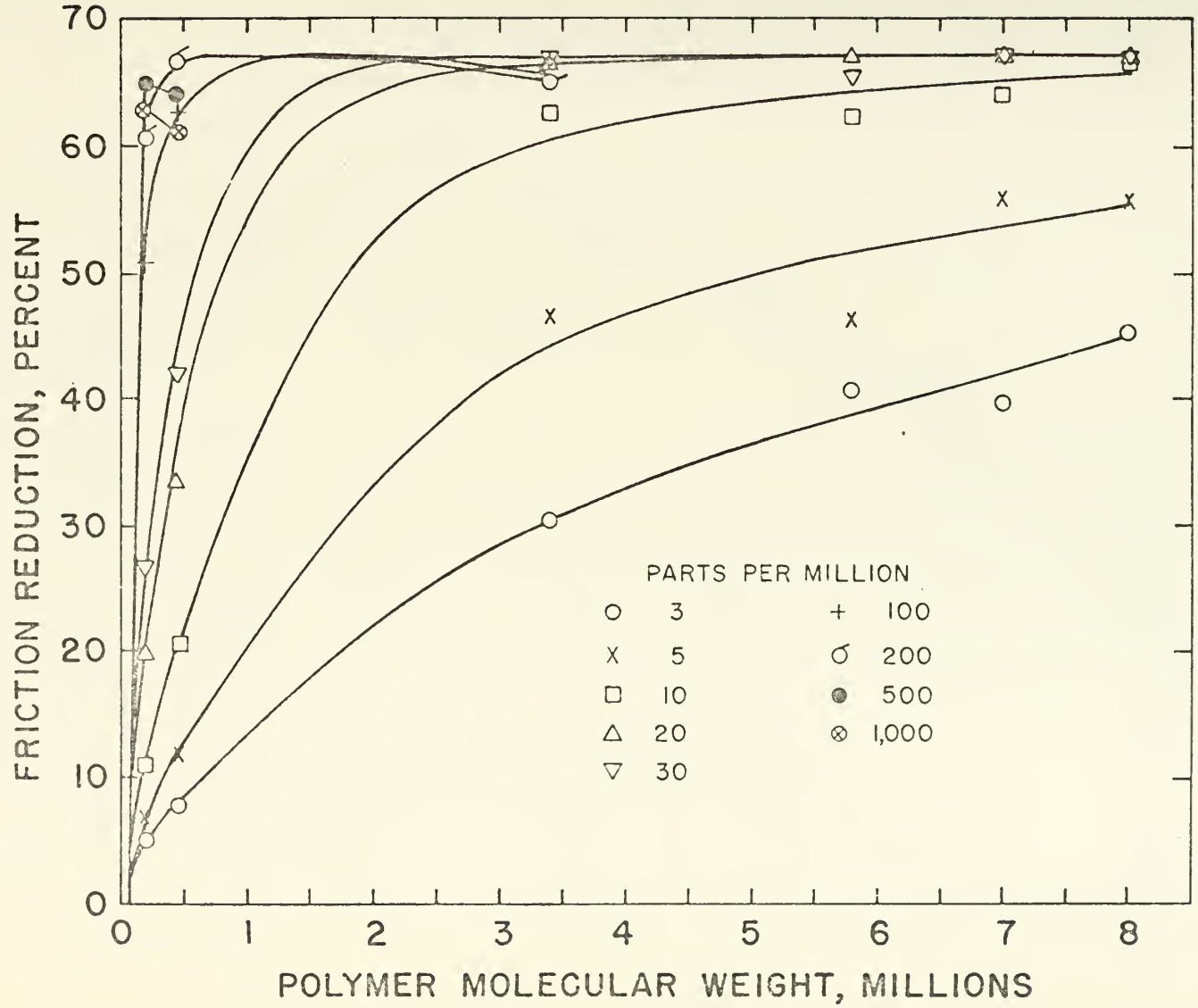


FIGURE 14: HOYT'S MOL. WT. ESTIMATION CHART

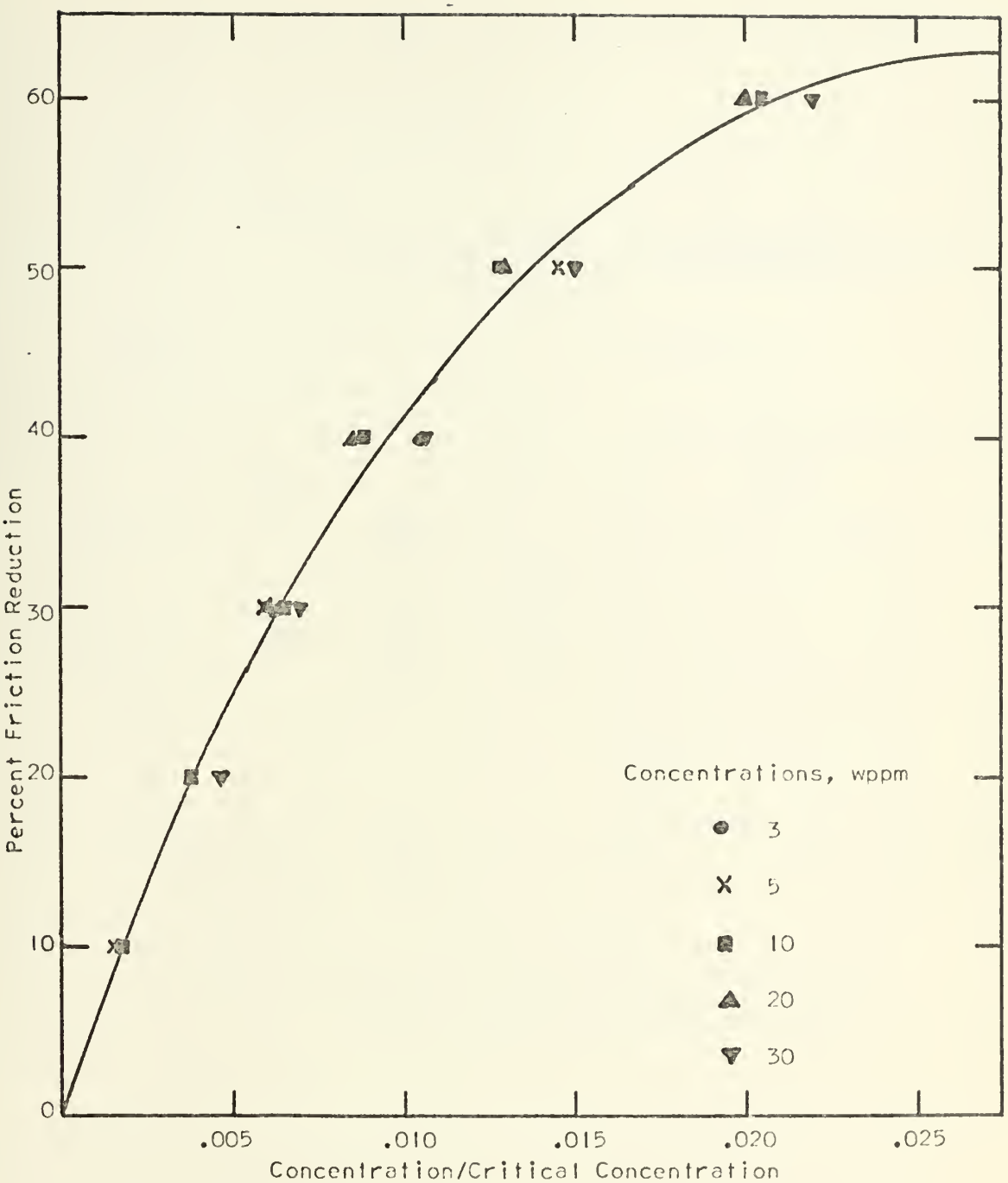


Figure 15: Volume equivalency normalization for Hoyt's Rheometer data. Concentration symbols correspond with Fig. 14.

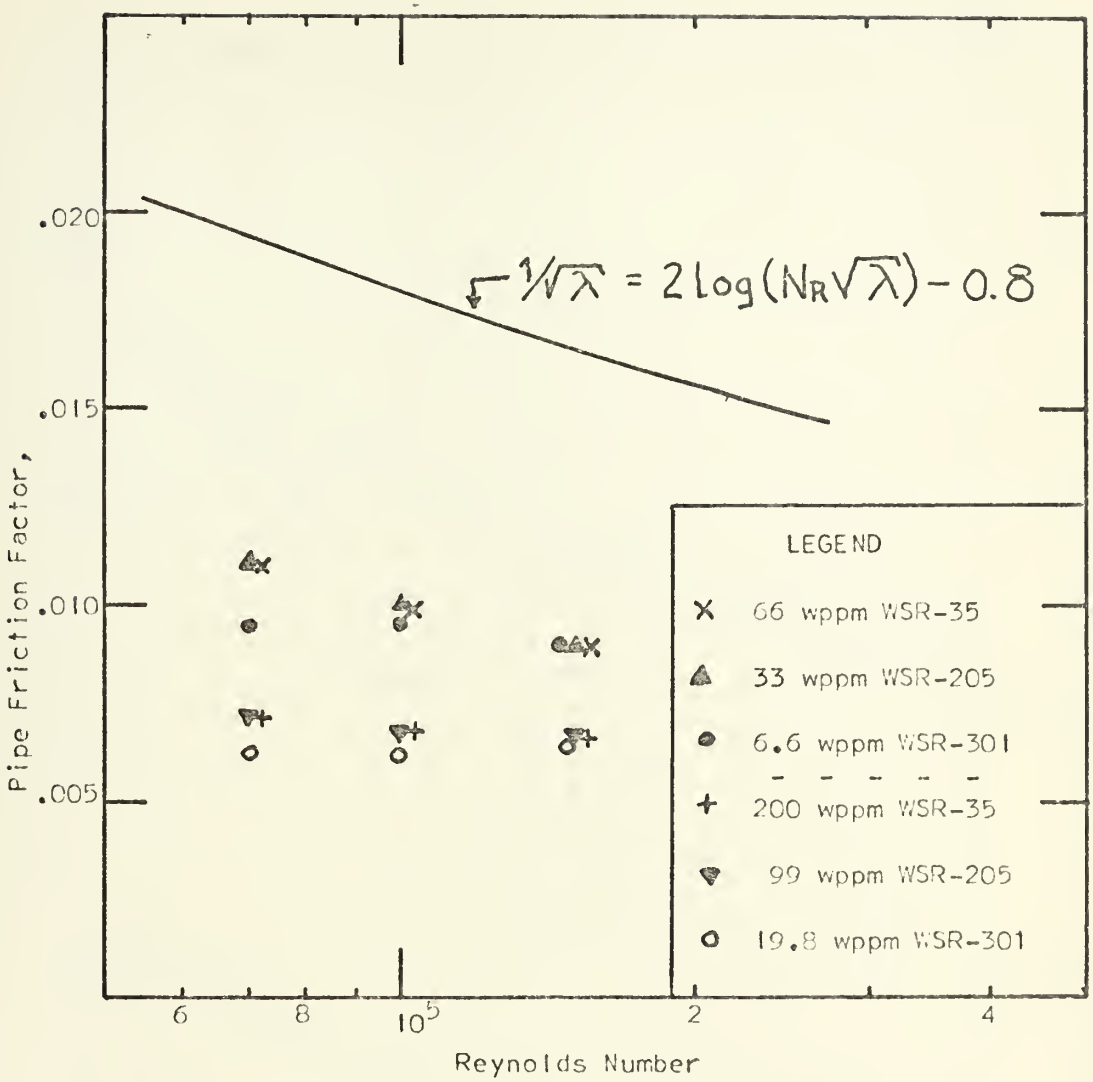


Figure 16: Frictional resistance for two sets of nearly volume equivalent solutions of polyethylene-oxide (Fabula's work).

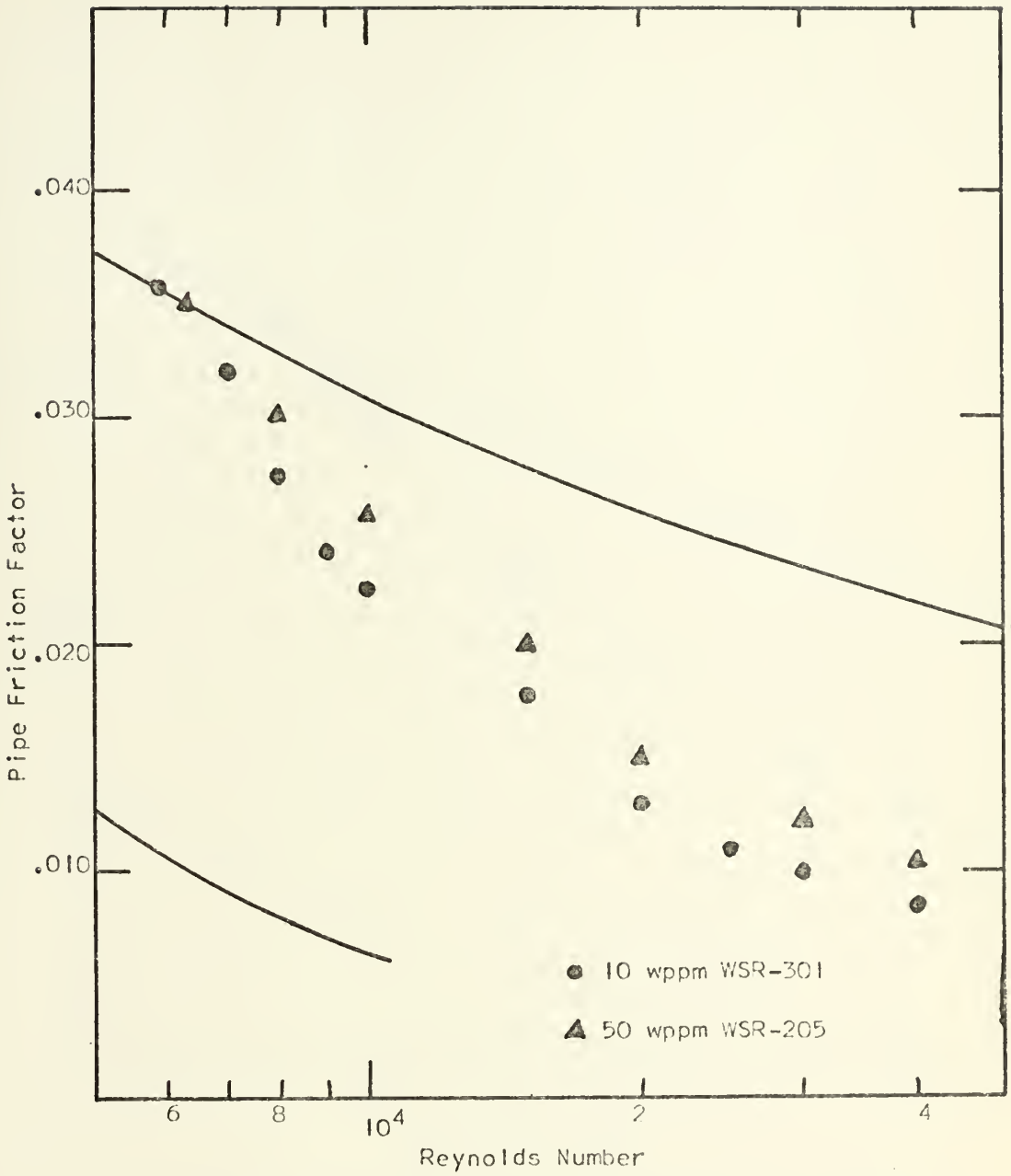


Figure 17: Frictional resistance for nearly volume equivalent solutions of polyethylene-oxide (Patterson's work). (55 wppm WSR-205 would have been volume equivalent to 10 wppm WSR-301 in Paterson's work.)

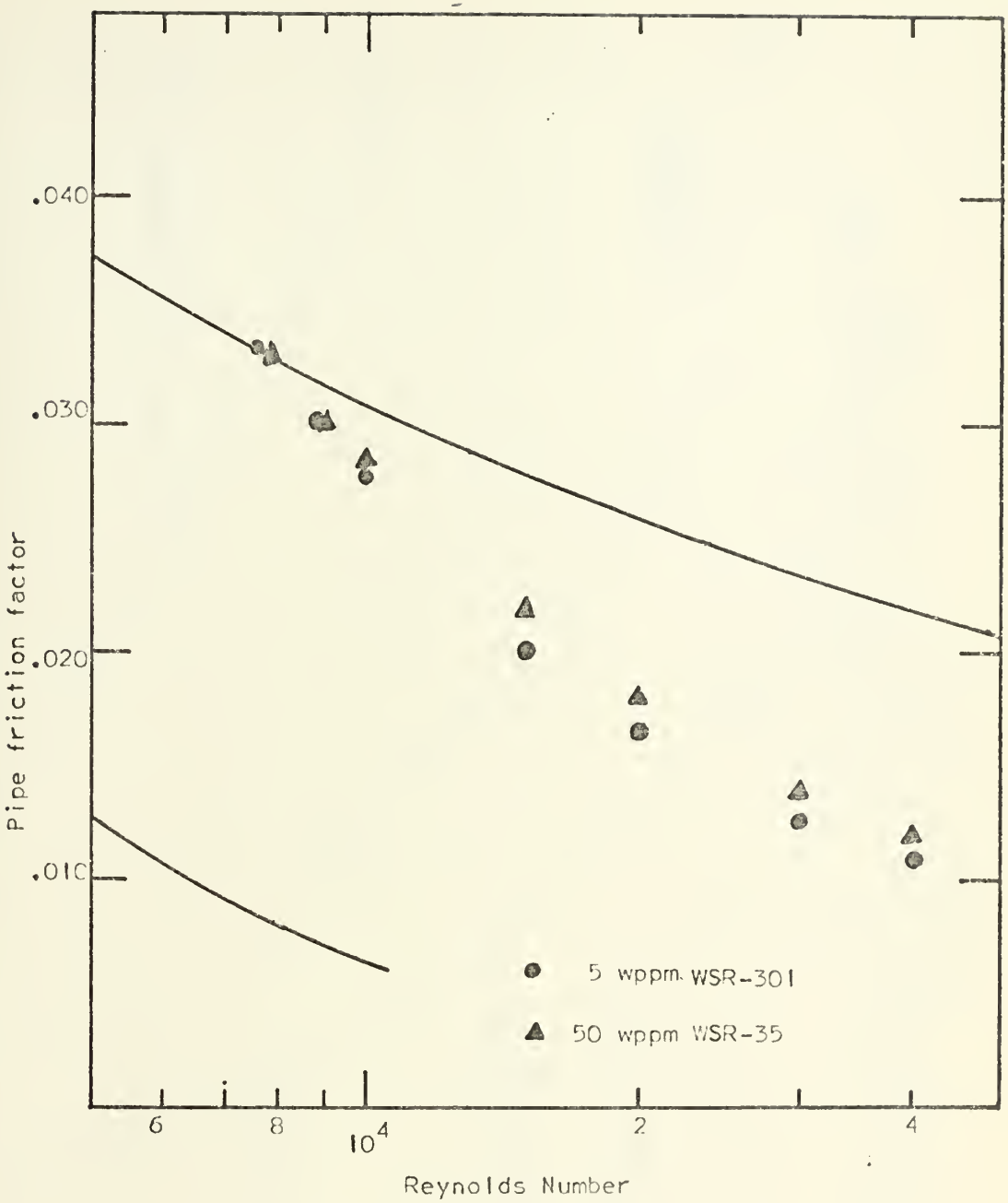


Figure 18: Frictional resistance for nearly volume equivalent solutions of polyethylene-oxide (Paterson's work). (55 wppm WSR-35 would have been volume equivalent to 5 wppm WSR-301 in Paterson's work.

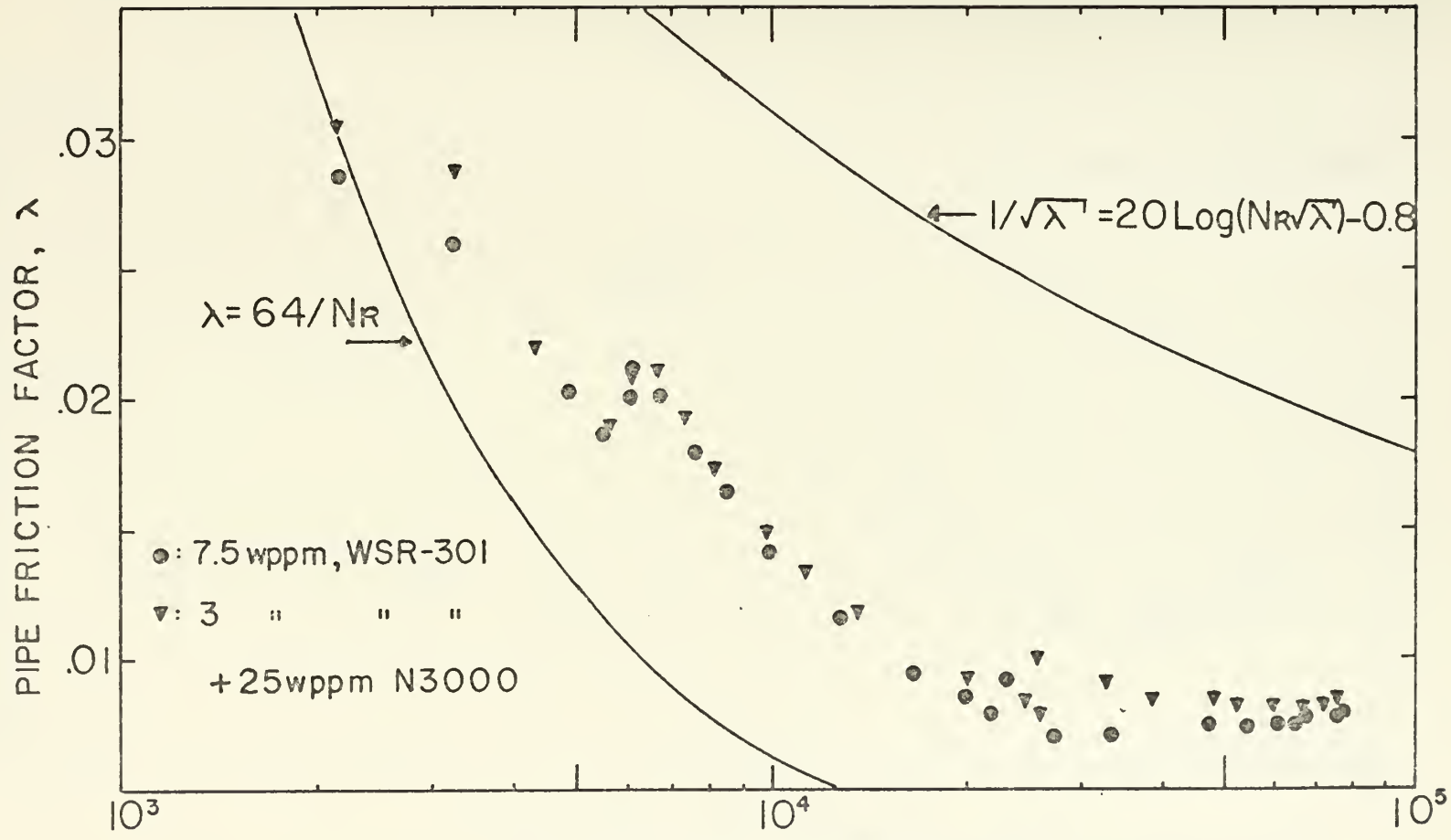


FIGURE 19: FRICTIONAL RESISTANCE FOR EQUIVALENT CONCENTRATIONS OF POLYETHYLENE OXIDE (PRESENT WORK)

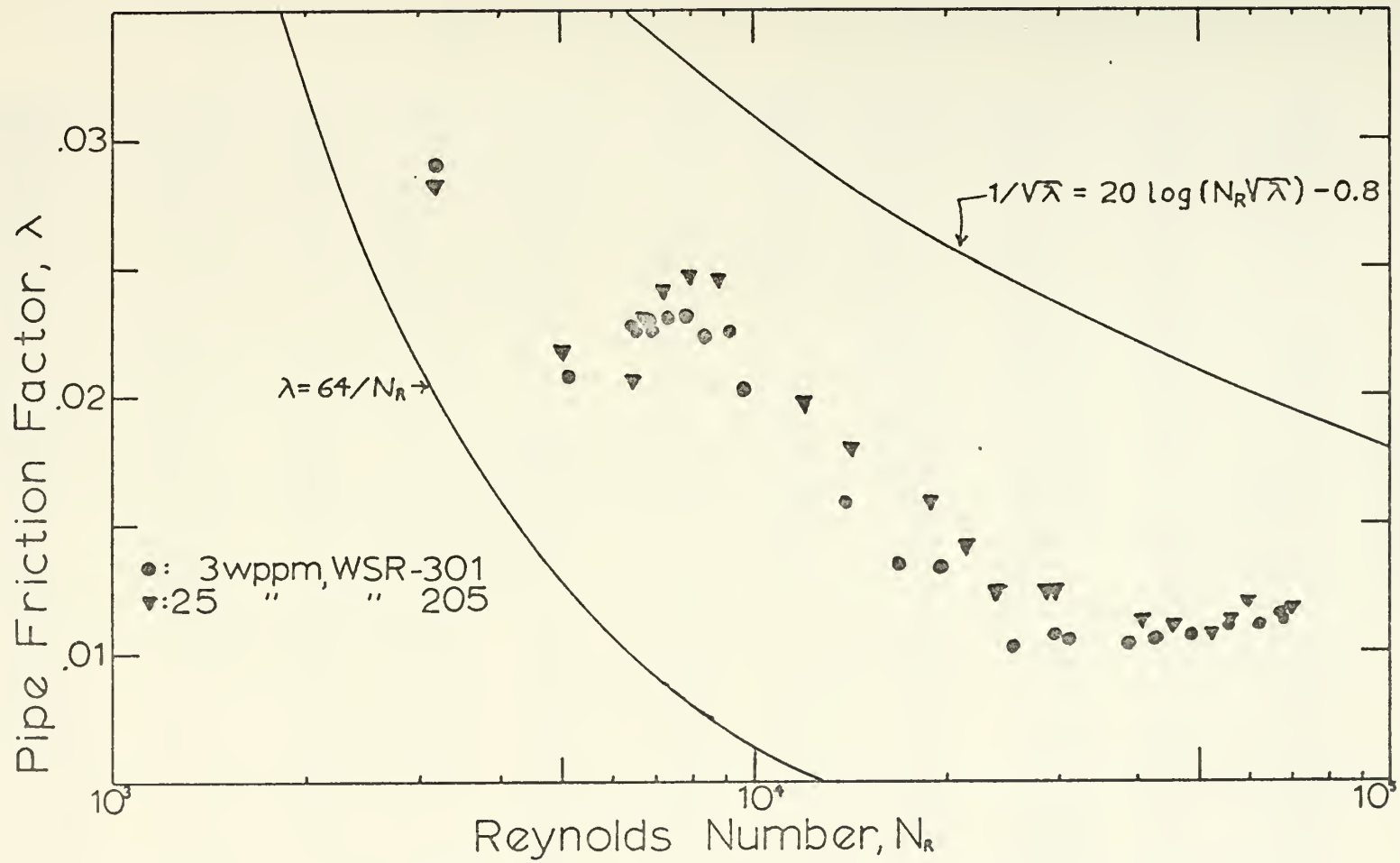


FIGURE 20: FRICTIONAL RESISTANCE FOR EQUIVALENT CONCENTRATIONS OF POLYETHYLENE OXIDE (PRESENT WORK)

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13. ABSTRACT
Pipe-friction factors for dilute aqueous polyethylene-oxide solutions in pipes of nominal diameters of ¼, 3/8, and 3/4 in. were measured over a two decade range of Reynolds numbers. In the transition region, the amount of drag reduction is dependent upon polymer concentration and wall shear stress as well as Reynolds number. For high Reynolds numbers, where the wall shear stress was high compared to the critical value, no diameter effect was noted. Intrinsic viscosity measurements, made on samples withdrawn from pipe flow, provided direct evidence that polymer degradation take place under flow conditions. Spectrographic measurements indicated that this degradation is mechanical (and not chemical). The relative volume of solution occupied by polymer molecules (represented by the volume of equivalent hydrodynamic spheres) is shown to be a dominant paramter governing the drag-reduction phenomenon for polyethylene-oxide solutions in pipe flow. It is further shown that the equivalent volume ratio may be used to normalize the pipe friction factors for various concentrations of different molecular-weight species of polyethylene-oxide.

14 KEY WORDS	LINK A		LINK B		LINK C	
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Polymer Degradation						
Transition						

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c.1 A correlation between friction reduction and molecular size for the flow of dilute aqueous polyethylene-oxide solutions in pipes.